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QUALITATIVE ANALYSIS
QUANTITATIVE ANALYSIS

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PREFACE

The International Library of Technology is the outgrowth of a large and increasing demand that has arisen for the Reference Libraries of the International Correspondence Schools on the part of those who are not students of the Schools. As the volumes composing this Library are all printed from the same plates used in printing the Reference Libraries above mentioned, a few words are necessary regarding the scope and purpose of the instruction imparted to the students of—and the class of students taught by—these Schools, in order to afford a clear understanding of their salient and unique features.

The only requirement for admission to any of the courses offered by the International Correspondence Schools, is that the applicant shall be able to read the English language and to write it sufficiently well to make his written answers to the questions asked him intelligible. Each course is complete in itself, and no textbooks are required other than those prepared by the Schools for the particular course selected. The students themselves are from every class, trade, and profession and from every country; they are, almost without exception, busily engaged in some vocation, and can spare but little time for study, and that usually outside of their regular working hours. The information desired is such as can be immediately applied in practice, so that the student may be enabled to exchange his present vocation for a more congenial one, or to rise to a higher level in the one he now pursues. Furthermore, he wishes to obtain a good working knowledge of the subjects treated in the shortest time and in the most direct manner possible.

In meeting these requirements, we have produced a set of books that in many respects, and particularly in the general plan followed, are absolutely unique. In the majority of subjects treated the knowledge of mathematics required is limited to the simplest principles of arithmetic and mensuration, and in no case is any greater knowledge of mathematics needed than the simplest elementary principles of algebra, geometry, and trigonometry, with a thorough, practical acquaintance with the use of the logarithmic table. To effect this result, derivations of rules and formulas are omitted, but thorough and complete instructions are given regarding how, when, and under what circumstances any particular rule, formula, or process should be applied; and whenever possible one or more examples, such as would be likely to arise in actual practice—together with their solutions—are given to illustrate and explain its application.

In preparing these textbooks, it has been our constant endeavor to view the matter from the student's standpoint, and to try and anticipate everything that would cause him trouble. The utmost pains have been taken to avoid and correct any and all ambiguous expressions—both those due to faulty rhetoric and those due to insufficiency of statement or explanation. As the best way to make a statement, explanation, or description clear, is to give a picture or a diagram in connection with it, illustrations have been used almost without limit. The illustrations have in all cases been adapted to the requirements of the text, and projections and sections or outline, partially shaded, or full-shaded perspectives, have been used, according to which will best produce the desired results. Half-tones have been used rather sparingly, except in those cases where the general effect is desired rather than the actual details.

It is obvious that books prepared along the lines mentioned must not only be clear and concise beyond anything heretofore attempted, but they must also possess unequaled value for reference purposes. They not only give the maximum of information in a minimum space, but this information is so ingeniously arranged and correlated, and the

indexes are so full and complete, that it can at once be made available to the reader. The numerous examples and explanatory remarks, together with the absence of long demonstrations and abstruse mathematical calculations, are of great assistance in helping one to select the proper formula, method, or process and in teaching him how and when it should be used.

The numerous questions and examples, with their answers and solutions, which have been placed at the end of each volume, will prove of great assistance to all who consult the Library.

The present volume is devoted to qualitative and quantitative analysis. The entire practical field of these subjects has been very carefully and thoroughly covered and the utmost pains have been taken to treat these subjects from the standpoint of the best practice in analytical laboratories. Every possible source of information has been explored and methods have been described to cover every case likely to arise in practice. This volume, used in connection with the volumes on inorganic and organic chemistry, should prove of invaluable assistance to all interested in analytical chemistry.

The method of numbering the pages, cuts, articles, etc. is such that each subject or part, when the subject is divided into two or more parts, is complete in itself; hence, in order to make the index intelligible, it was necessary to give each subject or part a number. This number is placed at the top of each page, on the headline, opposite the page number; and to distinguish it from the page number it is preceded by the printer's section mark (§). Consequently, a reference such as § 16, page 26, will be readily found by looking along the inside edges of the headlines until § 16 is found, and then through § 16 until page 26 is found.

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QUALITATIVE ANALYSIS.

(PART 1.)

INTRODUCTORY.

DEFINITIONS AND DESCRIPTIONS.

1. Analysis.—Analysis in its most general sense is the process of resolving more or less complex substances into simpler ones. It is, therefore, the reverse of synthesis, which consists in building up complex compounds from simpler ones. Analysis consists in breaking these compounds up into their component parts.

It is divided into *qualitative* and *quantitative analysis*.

Qualitative analysis is that branch of chemical science which considers the methods of determining the elements that compose a compound or mixture of compounds, without reference to the quantities of these elements which the substance contains.

Quantitative analysis takes up the subject where qualitative analysis leaves it, and determines the exact amount of each element in a substance.

2. Methods of Qualitative Analysis.—There are two methods of qualitative analysis, known as the wet method and the dry method. The *wet method*, as its name implies, deals with solutions, while the *dry method* deals with solids. In most cases, separate quantities of these solids may be put into solution, by methods to be described later, and to these portions the wet method may also be applied.

Each method has its advantages. The dry method is short and simple in many instances, requires but little apparatus, and, in case of some of the simpler substances, quickly yields a result. Its use is almost indispensable in some cases, but in many instances it only gives indications, which must be confirmed by the wet method.

The wet method has the advantage that it is almost universally applicable, and its results are absolutely certain if the work of obtaining them is properly done.

It is best to treat these two methods separately, so far as possible, in describing them and in the early part of the work, but after the student becomes familiar with them he will find it a great advantage to combine the two.

3. Abbreviations Used.—In analytical work, certain words occur so frequently that it is an advantage to use abbreviations for them. The following is a list of the most common ones used in this Course:

Ppt.—precipitate.	Conc.—concentrate.
Pptd.—precipitated.	Dil.—dilute.
Sol.—soluble.	O. F.—oxidizing flame.
Insol.—insoluble.	R. F.—reducing flame.

Sp. Gr.—specific gravity.

4. Reaction and Reagent.—A *reaction* is a chemical change, and the substance that produces this change is called a *reagent.*

ILLUSTRATION.—If a small quantity of silver nitrate solution be placed in a test tube and a few drops of hydrochloric acid added, a white precipitate of silver chloride is formed according to the equation:

$$AgNO_3 + HCl = AgCl + HNO_3$$

This change is called a reaction, and the hydrochloric acid, which produced the change, is a reagent.

The attention of the student is called to the fact that when a reagent is added to a metallic solution, the metallic compound formed is similar in composition to the reagent. Thus, if the reagent is a hydrate, a hydrate of the metal will be produced; a carbonate will form a carbonate of the metal; a sulphide produces a sulphide of the metal, etc. All

exceptions to this rule are given under "Deportment of the Metals with Reagents."

5. The Wet Method.—In wet analysis we determine the constituents of a solution of a substance by the reactions produced by certain common reagents. If there is but one metal in the solution, this becomes a very simple matter.

About half an inch of the solution to be tested is placed in a test tube and a small amount of the reagent is carefully added, drop by drop, while the place where the two liquids meet is closely watched. If no precipitate is formed, the test tube is emptied, washed well with common water, and rinsed out with distilled water. We are then ready to use a fresh portion of the solution and test in the same way with another reagent. *A dirty test tube must never be used. Neatness is essential in all successful analytical work.*

If we obtain a precipitate, the first thing to be noted is its color and general appearance. Its solubility may also help to establish its identity. If we wish to test its solubility in an excess of the reagent used to precipitate it, we pour out all but a small portion, and to this add more of the reagent. To test for its solubility in any other reagent, allow the precipitate to settle to the bottom of the tube as much as possible, pour off the supernatant liquid, retaining but a small quantity of the precipitate in the tube; to this add the desired reagent, shake it up, and observe the result.

By observing the reactions of a few common reagents and referring to the section on "Deportment of the Metals with Reagents," we can readily tell just what metal we have.

ILLUSTRATION.—If we add a few drops of hydrogen sulphide to a small quantity of a solution in a test tube and get a black precipitate, we know the metal is either silver, lead, mercurous, mercuric, or copper, for these are the only metals giving black precipitates with hydrogen sulphide. If to a fresh portion of the solution we add sodium hydrate and get a brown precipitate, we know the metal is silver, for that is the only one, of the five metals mentioned, that gives a brown precipitate with sodium hydrate.

When a result is obtained in this way it should always be confirmed by the other reactions given for the metal.

6. It will be noted that some of the metals form two series of compounds which differ widely from each other. Thus, mercury forms mercurous and mercuric compounds, which, in analytical chemistry, are treated as though they were salts of different metals.

APPARATUS NEEDED.

7. The only apparatus needed for the wet reactions, when there is but one metal in the solution, will be some test tubes, a set of reagents in properly labeled bottles, and a good burner. A Bunsen burner is preferable for this purpose, but where gas is not available, an alcohol lamp may be made to serve in its stead.

It is desirable that the student should become familiar with a few dry reactions in connection with the wet ones, and for this purpose he will need a blowpipe, a small piece of charcoal, a piece of platinum wire, a piece of platinum foil, a pair of forceps, a piece of blue glass, and, as the work proceeds, closed tubes, or matrasses, will be required.

8. The Burner.—A Bunsen burner, shown in Fig. 1, is made with a perforated metal cylinder *g* near the base, for regulating the air supply. In cases where the blowpipe is not used, a full supply of air is admitted, giving a non-luminous flame.

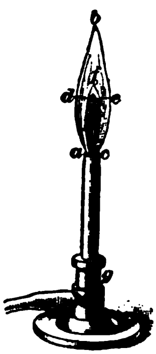

FIG. 1.

This consists of three parts: (1) An inner zone of unburned gas mixed with air, as seen at *afc*; (2) the outer mantle of burning gas mixed with an excess of air, shown at *abc*; and (3) the luminous cone *dfc*.

The different parts of this flame have two opposite effects. In the inner flame, the unburned gas, rich in carbon and hydrogen, tends to reduce the substance, while the outer flame, by heating the substance in the presence of the oxygen of the air, tends to oxidize it.

A substance to be reduced should be held in the luminous cone *dfc*, as reduction is most rapidly accomplished here.

A substance to be oxidized should be held just within the flame at *b*, as this is the point of most rapid oxidation. These points are meant when the reducing and oxidizing flames are mentioned.

If a substance is merely to be heated, it is held in the flame near the top, as this is the position of greatest heat. Some substances are volatilized and give a characteristic color to the flame, by which they may be recognized. For this purpose the substance is held in the lower part of the outer mantle *a b c*.

9. The Blowpipe.—By means of the blowpipe we obtain an intensely heated flame, which may be directed where we wish. There are several forms of blowpipe, the simplest being a small curved brass tube, terminating in an orifice about the size of a small needle. With this instrument, after blowing a while, the moisture which accumulates is blown into the flame. Several forms of blowpipe have been devised to avoid this. A good form is shown in Fig. 2. It consists of five parts. The mouthpiece *A* is usually made of hard rubber, and is pressed against the lips when in use. It fits into the tube *B*, which in turn is fitted into the moisture reservoir *C*. The tip holder *D* fits into the side of the moisture reservoir, and the tip *E* fits on to this.

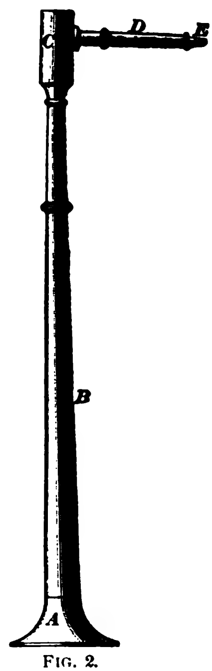

FIG. 2.

In using the blowpipe it is often necessary to blow a steady stream of air through it for several minutes, and the student should practice until he can do this before attempting any of the following operations. To accomplish this, the mouthpiece is pressed against the lips, and the cheeks inflated. Then, by means of the muscles of the cheeks, a steady stream of air is forced through the blowpipe, while we breathe through the nostrils. The air

should never be forced from the lungs, as by this means we cannot keep up a steady stream. This operation may seem difficult at first, but by practice it will soon become easy.

In blowpipe work a rather small, luminous flame, obtained by turning the metal cylinder so as to reduce the supply of air, is used, and from this we can obtain either an oxidizing or reducing flame, according to the method of using the blowpipe. By placing the tip of the blowpipe just outside

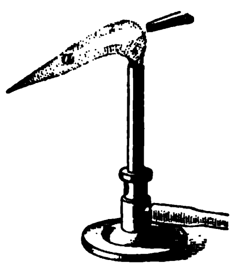

FIG. 3.

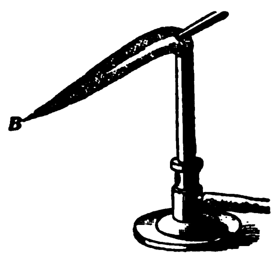

FIG. 4.

of the flame and blowing, we get a long, slightly luminous flame. A substance held at *a*, Fig. 3, is rapidly reduced by the unburned gas.

To get an oxidizing flame, the tip of the blowpipe should be placed just inside of the flame. Then, by blowing through it, a long, blue flame is obtained which will rapidly oxidize a substance held at the point *B*, Fig. 4, where it is intensely heated in the presence of an excess of air.

10. Charcoal.—In blowpiping, a small piece of fine-grained charcoal, made from soft wood, is largely used as a support. Common charcoal is very unsatisfactory, but the small blocks, for sale by all chemical dealers, are very good for this purpose. A small cavity is made in the charcoal, to hold the substance, and, after using, it must be well scraped out before the next operation.

11. Platinum Wire.—A short piece of fine platinum wire is essential in working by the dry method. It is well to heat one end of a small glass tube in the flame until it softens and begins to close; then, without

FIG. 5.

withdrawing it from the flame, insert one end of the wire and allow the glass to close over it, thus forming a handle which does not readily transmit heat. The result is shown in Fig. 5. The other end of the wire should be bent into a loop about $\frac{1}{12}$ inch in diameter.

This loop will serve to hold solid substances in the flame, to hold a drop of solution in the flame in order to observe if any color is thus imparted to it, and to hold the borax, or microcosmic bead, to be described later.

When not in use, it is a good plan to place the wire in dilute hydrochloric acid. Then, after burning it off, it is nearly always clean and ready for use. A good method of keeping the wire clean is to insert the glass handle in the perforation of a cork that is too large to go into a test tube, and by this means suspend the wire in a test tube containing hydrochloric acid, as shown in Fig. 6.

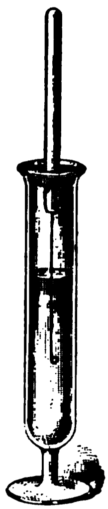
FIG. 6.

12. A small piece of platinum foil, which may be bent into the form of a spoon, and a pair of forceps with which to hold the foil, need no description. It is only necessary to say that platinum must never be heated in contact with the heavy metals, such as lead, mercury, etc., or their salts, for these will alloy with the platinum and ruin it.

13. Blue Glass.—A small piece of blue glass, which the operator may hold before his eye to look through at the colored flames produced by some of the metals, is indispensable when determining the alkalies.


FIG. 7.

14. Matrasses.—Closed tubes, or matrasses, are much used in analyzing solids, and may as well be described here. They are made in several forms. A good form may be made by cutting a piece of glass tubing, having an inside diameter of about $\frac{3}{16}$ of an inch,

into pieces about 3½ inches long, and holding one end of each piece in the flame till it softens and closes. The result is shown in Fig. 7.

Solids may be dropped into this tube and heated at the closed end, by holding it in the flame. To protect the fingers from the heat, the tube may be held in the forceps, or a piece of paper may be folded and wrapped around it near the top, thus serving as a holder.

REAGENTS.

15. Preparation of Solutions.—In the outfit that we furnish to students, all reagents except nitric, hydrochloric, and sulphuric acids, and ammonium hydrate—or ammonia, as it is commonly called—are of the proper strength for use. Those mentioned are needed in two strengths, concentrate and dilute. The student is furnished with the concentrate solutions, and from these he can make the dilute solutions by adding a small portion of each to four times its volume of water, and mixing them well. The sulphuric acid must be added to the water slowly while the solution is constantly stirred, on account of the heat generated. In this, as in every case where water is mentioned, distilled water should be used. When a reagent is mentioned, the dilute solution is always meant unless the concentrate solution is specified.

For the benefit of students that do not obtain our outfit, the following directions are given for making up reagents:

Chemically pure substances should be used in every case.

Ammonium Carbonate.—Dissolve 100 grams of the solid in 300 cubic centimeters of water and 100 cubic centimeters of concentrate ammonium hydrate, and dilute to 500 cubic centimeters with water.

Ammonium Chloride.—Dissolve 100 grams of the dry salt in a sufficient amount of water—say 400 cubic centimeters—and then add water to make 500 cubic centimeters of solution.

Ammonium Oxalate.—Add to 25 grams of the salt,

sufficient water to make 500 cubic centimeters of solution. Allow it to stand until it dissolves, shaking it occasionally.

Sodium Hydrate.—Dissolve 40 grams of the solid in water, and dilute this solution to 500 cubic centimeters with water.

Sodium Carbonate.—Dissolve 100 grams of the dry salt, or 270 grams of the crystals, in sufficient water to make 500 cubic centimeters of solution.

Sodium Phosphate.—Dissolve 50 grams of acid sodium phosphate $Na_2HPO_4, 12H_2O$ in sufficient water to make 500 cubic centimeters of solution.

Potassium Chromate.—Dissolve 50 grams in water and add water to this solution to make it up to 500 cubic centimeters.

Potassium Ferricyanide.—To 50 grams of the solid, add water enough to make 500 cubic centimeters of solution.

Potassium Ferrocyanide and Potassium Cyanide.—These are made of the same strength and in the same manner as potassium ferricyanide.

Potassium Iodide.—Dissolve 20 grams of the crystallized salt in 500 cubic centimeters of water.

Barium Chloride.—Dissolve 25 grams of the solid in 500 cubic centimeters of water.

Silver Nitrate.—Dissolve 20 grams of the crystals in 500 cubic centimeters of water.

Lead Acetate.—Dissolve 50 grams of the dry salt in water to which 1 cubic centimeter of acetic acid has been added, using water enough to make 500 cubic centimeters of the solution.

Mercuric Chloride.—Dissolve 25 grams of the crystals in 500 cubic centimeters of water.

Stannous Chloride.—Dissolve 25 grams of the solid stannous chloride in 75 cubic centimeters of concentrate hydrochloric acid, and enough water to make 500 cubic centimeters of solution. Some metallic tin should be kept in the solution, which should be kept in a tightly stoppered bottle.

Ferrous Sulphate.—To 75 grams of the crystals, add

water enough to make 500 cubic centimeters of solution. To this add about 1 cubic centimeter of concentrate sulphuric acid and a little metallic iron, and keep the solution from the air.

Cobalt Nitrate.—Dissolve 50 grams of the crystallized salt in water, and dilute the solution to 500 cubic centimeters with water.

Tartaric Acid.—Dissolve 100 grams of the solid tartaric acid in water sufficient to make 500 cubic centimeters of solution.

Acetic Acid.—Dilute the 33-per-cent. acid with twice its volume of water to make the dilute acid.

Hydrogen Sulphide.—Generate the gas as described in Experiment 50, Art. **105,** *Inorganic Chemistry*, Part 1, and lead it into water until the water is saturated, when it is ready for use. The solution should be protected from the air.

Ammonium Sulphide.—Lead hydrogen-sulphide gas into a bottle two-thirds full of concentrate ammonium hydrate, until it is saturated, which is indicated by the bubbles coming through the liquid undiminished in size. Fill the bottle with concentrate ammonia and mix it well. Before using, dilute this with twice its volume of water.

Yellow Ammonium Sulphide.—This is made by adding a small quantity of flowers of sulphur to the common ammonium sulphide and shaking until dissolved. Enough sulphur should be added to give the solution an amber color.

Ammonium Sulphate.—Dissolve 50 grams of the solid ammonium sulphate in sufficient water to make 500 cubic centimeters of solution. Its principal use is in separating strontium and calcium.

Magnesium Sulphate.—Dissolve 50 grams of the crystallized salt in water enough to make 500 cubic centimeters of the solution.

Calcium Sulphate.—A saturated solution is always used. It is prepared by repeatedly shaking up some finely powdered calcium sulphate in a bottle of water, taking care to have more of the sulphate than the water will dissolve.

Allow it to stand for some time and decant the clear liquid for use.

Barium Hydrate.—To 25 grams of pure barium-hydrate crystals, add sufficient water to make 500 cubic centimeters of solution, and dissolve by the aid of heat. Filter into a bottle provided with a good stopper, and close the bottle at once to protect the solution from the air. The filtration is performed as directed in Art. **99,** *Theoretical Chemistry.*

Acid Sodium Tartrate.—A saturated solution is used. It is prepared by placing in a bottle, about three-fourths filled with water, a little more of the solid salt than will be dissolved, and shaking repeatedly. Allow it to settle, and decant the clear solution as it is needed.

Ammonium Molybdate.—This may be made by dissolving 25 grams of powdered ammonium molybdate in 75 cubic centimeters of concentrate ammonia, by the aid of heat. Pour this solution slowly, and with constant stirring, into a mixture of 300 cubic centimeters of concentrate nitric acid and 200 cubic centimeters of water. This solution should be allowed to stand for at least 24 hours before using.

The directions in most cases are given for making 500 cubic centimeters, merely because that is a convenient quantity. More or less of any reagent may just as well be made, provided the proportions are not altered.

DEPORTMENT OF THE METALS WITH REAGENTS.

INTRODUCTORY.

16. We now come to the *deportment*, or *behavior*, of the metals with reagents. The student should not attempt to commit all these reactions to memory, but should make himself so familiar with them that he can readily distinguish any of the metals by their reactions. For this purpose only a

few reactions will generally be necessary, but the results thus obtained should always be confirmed by all the others given.

So far as possible, it is desirable to perform each of the following operations, using known solutions before attempting to analyze unknown ones.

The student will soon learn to form groups of the metals that are precipitated by the different reagents; as, for instance, he will learn that only three metals, silver, lead, and mercury, in the mercurous form, are precipitated by hydrochloric acid; five by sulphuric acid, etc. In this he will be assisted by the table at the end of this section.

Each student should keep, in a note book, a complete record of all work done. It is especially important that anything that is not understood at the time should be recorded in this book.

SILVER.

17. Silver is a white metal that fuses on the charcoal before the blowpipe, forming a bright, metallic globule. It does not volatilize, and no incrustation* is formed. To perform this and similar operations, a piece of the metal, about twice as large as the head of a pin, is placed in a small cavity in the charcoal, made to hold it, and the blowpipe flame is directed upon it. In all blowpipe work, only small quantities of the substance treated must be used. Silver is only very slowly acted upon by hydrochloric acid, forming insoluble silver chloride $AgCl$. It dissolves slowly in dilute sulphuric acid, forming silver sulphate, and dissolves very readily in nitric acid, forming silver nitrate $AgNO_3$.

This solution may be used for the silver reactions, but it is best to make a solution for this purpose from silver-nitrate crystals. In the case of each of the metals, directions are given for making a solution. Of course, any other solution would give the same reactions, but the solution given is most easily made, and is in the form in which we are most likely to find the metal in actual analysis.

* By an incrustation is meant a deposit on the charcoal surrounding, or near, the substance heated.

A silver solution may be made by dissolving about 2 grams of silver-nitrate crystals in 100 cubic centimeters of water and adding a drop or two of nitric acid. The acid is best added by means of a dropper, which may be made by drawing out a glass tube, and cutting it as shown in Fig. 35, *Theoretical Chemistry*. When the small end of this tube is dipped into the liquid, the liquid, of course, enters it, and may be retained in the tube by pressing the finger closely upon the upper end. If the finger is removed, the liquid will be released, and by this means we can get any amount of liquid we wish.

18. Reactions.—A silver solution gives the following reactions:

1. *Ammonium hydrate*, if added in very small amount to a rather strong neutral solution of silver that does not contain ammonium compounds, precipitates brown silver oxide Ag_2O, which is very soluble in an excess of the reagent. As silver oxide is very soluble in ammonia, and its formation is prevented by the presence of ammonium compounds, no precipitate is usually obtained. Most silver solutions contain free acid, hence, when ammonia is added, ammonium compounds are formed, which prevent the formation of a precipitate.

2. *Sodium hydrate* precipitates brown silver oxide Ag_2O, which is insoluble in an excess of the reagent, but very soluble in ammonia.

3. *Ammonium carbonate* precipitates white silver carbonate Ag_2CO_3, which is easily soluble in excess.

4. *Sodium carbonate* gives a white precipitate of silver carbonate Ag_2CO_3, which is insoluble in excess, but is readily soluble both in nitric acid and ammonia.

5. *Hydrogen sulphide* precipitates black silver sulphide Ag_2S, which is not easily dissolved in cold dilute acids, but soluble in boiling dilute nitric acid.

6. *Ammonium sulphide* gives the same precipitate as hydrogen sulphide. It may be well at this point to state that in every case where hydrogen sulphide gives a precipitate,

ammonium sulphide gives the same. The reverse, however, is not true, as we shall see later.*

7. *Hydrochloric acid* precipitates white silver chloride $AgCl$, which slowly changes to brown upon exposure to sunlight. It is insoluble in nitric acid, but is readily soluble in ammonium hydrate, from which solution it is reprecipitated by nitric acid.

8. *Copper* deposits metallic silver from its solutions. If a small piece of copper be dropped into a silver solution, it soon becomes gray, owing to the silver that is deposited on it. Upon rubbing, it becomes bright.

9. *Sodium phosphate* precipitates yellow silver phosphate Ag_3PO_4, which is soluble in both nitric acid and ammonium hydrate.

10. *Potassium cyanide* precipitates white silver cyanide $AgCN$, which is soluble in excess of the reagent and in ammonium hydrate, but insoluble in nitric acid.

LEAD.

19. Lead is a soft, white metal when freshly cut, but soon tarnishes in the air. It fuses easily on the charcoal before the blowpipe, giving the flame a pale, bluish tinge, and depositing a yellow incrustation of the oxide PbO on the charcoal. This incrustation is volatile, and may be driven from place to place on the charcoal by directing the blowpipe flame upon it.

Lead is only slightly acted upon by hydrochloric or sulphuric acid. It is best dissolved by adding a little concentrate nitric acid and then an equal volume of water and heating if necessary.

A solution of the nitrate $Pb(NO_3)_2$ may be made by dissolving about 3 grams of the solid lead nitrate in 100 cubic

* The reason for this is that sulphides of some of the metals are not precipitated from acid solutions, but are precipitated from alkaline ones. Ammonium sulphide, being a strong alkali, renders the solution alkaline, and the precipitate is formed.

centimeters of water and adding a drop or two of nitric acid.

20. Reactions.—A lead solution gives the following reactions:

1. *Ammonium hydrate* precipitates white lead hydrate $Pb(OH)_2$, which is insoluble in excess of the reagent.

2. *Sodium hydrate* precipitates white lead hydrate $Pb(OH)_2$, which is easily soluble in excess of the reagent, forming a solution of $Pb(ONa)_2$.

3. *Ammonium carbonate* precipitates white basic lead carbonate of varying composition.

4. *Sodium carbonate* gives the same precipitate as ammonium carbonate.

5. *Hydrogen sulphide* precipitates black lead sulphide PbS, which is insoluble in dilute acids and alkalies when cold, but is dissolved in boiling dilute nitric acid. Hot concentrate nitric acid converts it into white insoluble lead sulphate. If we wish to obtain this white sulphate, there must be no liquid present to dilute the acid.

6. *Ammonium sulphide* gives the same reactions as hydrogen sulphide.

7. *Hydrochloric acid* precipitates white lead chloride $PbCl_2$, which is slightly soluble in cold, and readily soluble in hot, water. If this hot solution be allowed to cool, the lead chloride separates in long, white crystals.

8. *Sulphuric acid* precipitates white lead sulphate $PbSO_4$, which is nearly insoluble in dilute acids, but may be dissolved by adding tartaric acid and then a slight excess of concentrate ammonia, and heating.

9. *Potassium chromate* precipitates yellow lead chromate $PbCrO_4$, which is soluble in sodium hydrate, from which solution it is reprecipitated by nitric acid.

10. *Potassium iodide* precipitates yellow lead iodide PbI_2, which is soluble in boiling water. Upon cooling, it separates from this solution in yellow crystals.

11. *Potassium cyanide* precipitates white lead cyanide $Pb(CN)_2$, which is insoluble in excess of the reagent, but is soluble in nitric acid.

MERCURY.

21. Mercury is a heavy, white liquid. It is but slightly acted upon by hydrochloric or sulphuric acid, but dissolves readily in nitric acid. It forms two series of compounds, known as mercur*ous* and mercur*ic*. When mercury is dissolved in the cold, in dilute nitric acid, if there is an excess of mercury present, mercurous nitrate $Hg_2(NO_3)_2$ is obtained. If it is dissolved in an excess* of hot concentrate nitric acid, mercuric nitrate $Hg(NO_3)_2$ is formed.

These solutions could be properly diluted and used for the reactions, but it is better to make up solutions as directed later.

MERCUROUS COMPOUNDS.

22. A solution for the mercurous reactions may be made by adding to 4 grams of solid mercurous nitrate 100 cubic centimeters of water, and about 1 cubic centimeter of dilute nitric acid; then add a few drops of metallic mercury, and heat gently, if necessary. A high temperature must be avoided, and some metallic mercury should remain in the solution, or it is likely to be partly changed to a mercuric compound.

23. Reactions.—A mercurous solution gives the following reactions:

1. *Ammonium hydrate* precipitates black amido-mercurous nitrate $Hg_2NH_2NO_3$ from this solution. The precipitate is insoluble in an excess of the reagent.

2. *Sodium hydrate* precipitates black mercurous oxide Hg_2O, which is insoluble in an excess of the reagent.

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* By an excess of a reagent is meant more than is required to accomplish a certain object. When we speak of precipitating a metal with an excess of a certain reagent, we mean to use more of the reagent than would be required to unite with the metal to form a precipitate. To render an alkaline solution acid, with an excess of a certain acid, we would use more of that acid than would be required to neutralize the alkali. When we say that a precipitate is soluble in an excess of a reagent, we mean that when more of the reagent than is required to form the precipitate is added, it dissolves the precipitate at first formed.

3. *Ammonium carbonate* gives a white precipitate, which rapidly changes to gray, and finally to black, upon standing.

4. *Sodium carbonate* gives a white precipitate, more or less colored with yellow, owing to the fact that mercurous solutions nearly always contain small quantities of mercuric compounds The carbonate precipitates are not important in determining mercurous compounds.

5. *Hydrogen sulphide* precipitates black mercuric sulphide HgS together with some free mercury. The precipitate is not dissolved by any dilute acid, but dissolves slowly in hot concentrate hydrochloric acid, and readily in aqua regia.

In this and similar operations, where aqua regia is used as a solvent, add to a small quantity of the substance a half-dozen drops of concentrate nitric acid, and then from two to three times as much concentrate hydrochloric acid, and heat if necessary. This mixture of concentrate acids is known as aqua regia. It acts as a powerful solvent, dissolving many substances that are not attacked by ordinary acids. It is the only solvent for gold and platinum.

Boiling concentrate nitric acid converts the black mercuric sulphide into a white, insoluble compound. The same precautions must be taken as described in Art. **20**, 5.

6. *Hydrochloric acid* precipitates white mercurous chloride Hg_2Cl_2, which is insoluble in cold dilute acids, is slightly acted upon by hot concentrate acids, and is readily dissolved by aqua regia. Ammonia converts this white chloride into black amido-mercurous chloride Hg_2NH_2Cl.

7. *Potassium chromate* precipitates brick-red basic mercurous chromate, which dissolves with difficulty in nitric acid.

8. *Potassium iodide* in very small quantities precipitates yellowish-green mercurous iodide Hg_2I_2. If a little more of the reagent is added and it is allowed to stand, the precipitate changes into metallic mercury and bright-red potassium mercuric iodide $HgI_2(KI)_2$.

9. *Sulphuric acid* precipitates white mercurous sulphate Hg_2SO_4, which is dissolved with some difficulty in nitric acid.

10. *Stannous chloride*, when added in a very small amount,

precipitates white mercurous chloride Hg_2Cl_2. A little more of the reagent partly reduces this, giving a gray mixture of mercurous chloride and metallic mercury. An excess of stannous chloride reduces the whole to a dark-gray, almost black, precipitate of finely divided metallic mercury. The white precipitate is seldom seen, but the gray mixture usually is formed at once.

11. *Sulphurous acid* precipitates gray metallic mercury.

12. *Copper*, when placed in a mercurous solution, precipitates metallic mercury, which forms a gray coating on the copper. This may be rendered bright by rubbing with a dry cloth, and is driven off by heat.

MERCURIC COMPOUNDS.

24. The solution of mercuric nitrate, which is obtained when mercury is dissolved in an excess of hot concentrate nitric acid, may be used for the following reactions, after having the excess of acid evaporated off, and being properly diluted with water; or a solution for the purpose may be made by diluting some of the mercuric-chloride solution used as a reagent with a little more than its own volume of water and adding 2 or 3 drops of hydrochloric acid. But it is best to make up a solution for this purpose by dissolving about 2 grams of dry mercuric nitrate in 100 cubic centimeters of water to which 2 or 3 drops of concentrate nitric acid have been added.

25. Reactions.—A mercuric solution gives the following reactions:

1. *Ammonium hydrate* precipitates white amido-mercuric nitrate $HgNH_2NO_3$, which is somewhat soluble in an excess of the reagent, and is readily dissolved by acids.

2. *Sodium hydrate* precipitates a brown basic salt, if a very small quantity of the reagent is used. If more of the reagent is added, yellow mercuric oxide HgO is formed. This is easily dissolved by warm dilute acids.

3. *Ammonium carbonate* produces a white precipitate, which is soluble in ammonia and in acids.

4. *Sodium carbonate* precipitates a reddish-brown basic carbonate, probably $HgCO_3, 3HgO$.

5. *Hydrogen sulphide* gives a white precipitate when a very small amount of reagent is added. If we continue to add the reagent, the precipitate changes to yellow, reddish-brown, and finally to black HgS. The white precipitate at first formed is $2HgS, Hg(NO_3)_2$, and this mixed with the black HgS, in varying proportions, probably causes the intermediate colors. The black HgS is insoluble in alkalies, and in the acids used separately, but is dissolved by aqua regia.

6. *Ammonium sulphide* gives the same precipitate as hydrogen sulphide.

7. *Potassium iodide* precipitates red mercuric iodide HgI_2, which is soluble in excess of the reagent.

8. *Stannous chloride* precipitates, at first, white mercurous chloride Hg_2Cl_2. An excess of the reagent reduces this to gray metallic mercury.

9. *Copper* precipitates the mercury from mercuric solutions the same as from mercurous ones.

COPPER.

26. Copper is a rather hard metal, with a peculiar red color. It is malleable and ductile, and fuses with difficulty. It is scarcely attacked by hydrochloric or sulphuric acid, but is readily dissolved in nitric acid. A good solution for the following reactions is made by dissolving from 1½ to 2 grams of copper-sulphate crystals $CuSO_4, 5H_2O$ in 100 cubic centimeters of water, and adding a drop or two of dilute sulphuric acid.

27. Reactions.—A copper solution gives the following reactions:

1. *Ammonium hydrate* precipitates a light-blue basic compound, which is very soluble in excess, giving the

solution a deep-blue color, owing to the formation of a soluble basic copper-ammonium sulphate.

2. *Sodium hydrate* precipitates light-blue copper hydrate $Cu(OH)_2$, which is insoluble in an excess of the reagent, but soluble in ammonia and in acids. The precipitate is changed by boiling into black, hydrated copper oxide, probably $2CuO,Cu(OH)_2$.

3. *Ammonium carbonate* gives the same reaction as ammonium hydrate.

4. *Sodium carbonate* precipitates blue basic copper carbonate $CuCO_3,Cu(OH)_2$, which is converted into black, hydrated copper oxide by boiling.

5. *Hydrogen sulphide* precipitates black copper sulphide CuS, which is easily soluble in warm nitric acid or potassium cyanide.

6. *Ammonium sulphide* gives the same precipitate as hydrogen sulphide.

7. *Potassium cyanide* precipitates greenish-yellow copper cyanide $Cu(CN)_2$, which is easily soluble in excess of the reagent, forming a colorless solution. The copper is not precipitated from this solution by hydrogen sulphide.

8. *Potassium ferrocyanide* precipitates reddish-brown copper ferrocyanide $Cu_2Fe(CN)_6$, which is insoluble in dilute acids.

9. If a small piece of solid copper chloride, or a drop of the solution, supported on the loop of a platinum wire, be held in the flame of a Bunsen burner, it imparts a blue color to the flame, while the other volatile compounds of copper color the flame green.

10. *Iron*, when placed in a copper solution, slowly becomes coated with the copper. If the solution is strong and slightly acid, this action becomes quite rapid.

CADMIUM.

28. Cadmium is a white, rather soft metal, which easily fuses on the charcoal before the blowpipe, depositing a brown incrustation of the oxide CdO, which is volatile, and

may be driven from place to place on the charcoal by directing the blowpipe flame upon it. Cadmium is slowly dissolved in hydrochloric or sulphuric acid, but is much more readily dissolved by nitric acid, giving a solution of cadmium nitrate $Cd(NO_3)_2$. This solution may be used for the reactions, after boiling off the excess of acid and diluting with water, but it is better to make a solution for this purpose by dissolving about 2 grams of cadmium nitrate crystals in 100 cubic centimeters of water and adding a drop of nitric acid.

29. Reactions.—A cadmium solution gives the following reactions:

1. *Ammonium hydrate* does not usually give a precipitate in ordinary cadmium solutions, but if a single drop of dilute ammonia is added to a rather strong neutral solution, a white precipitate of cadmium hydrate $Cd(OH)_2$ is obtained. This precipitate is very soluble in ammonia, and its formation is prevented by the presence of ammonium salts.

2. *Sodium hydrate* precipitates white cadmium hydrate $Cd(OH)_2$, which is insoluble in excess of the reagent.

3. *Ammonium carbonate* precipitates white cadmium carbonate $CdCO_3$, which is quite readily dissolved in an excess of the ordinary reagent, owing to the ammonia which it contains. The precipitate would be but slightly attacked by the carbonate alone.

4. *Sodium carbonate* precipitates white cadmium carbonate $CdCO_3$, which is insoluble in excess of the reagent, but soluble in ammonia, potassium cyanide, and acids. Heating the solution aids in the formation of the precipitate.

5. *Hydrogen sulphide* precipitates yellow cadmium sulphide CdS, which is insoluble in cold dilute acids, ammonia, ammonium sulphide, and potassium cyanide, but is dissolved by boiling dilute acids.

6 *Ammonium sulphide* gives the same reaction as hydrogen sulphide.

7. *Potassium chromate* precipitates yellow basic cadmium chromate, which is insoluble in sodium hydrate, but is dissolved by nitric acid.

8. *Potassium cyanide* does not ordinarily produce a precipitate, but forms a soluble double cyanide of potassium and cadmium $Cd(CN)_2(KCN)_2$, from which yellow cadmium sulphide (CdS) may be precipitated by hydrogen sulphide.

BISMUTH.

30. Bismuth is a rather hard, brittle metal, having a white color with a slightly reddish tinge. It fuses easily on the charcoal before the blowpipe, forming a metallic globule, and depositing a yellow incrustation of bismuth oxide Bi_2O_3. It is not attacked by dilute hydrochloric and sulphuric acids, but is readily dissolved in nitric acid, forming bismuth nitrate $Bi(NO_3)_3$. This solution may be used for the reactions, after diluting with water and keeping just enough nitric acid present to hold the salt in solution; or, we may make a solution for the purpose by dissolving about 2 grams of bismuth nitrate in about 1 cubic centimeter of dilute nitric acid, and 15 or 20 cubic centimeters of water. If this does not form a clear solution after heating, add nitric acid, a few drops at a time, until it clears up. Then dilute to 100 cubic centimeters with water. If a precipitate forms during dilution, add just nitric acid enough to dissolve it.

31. Reactions.—A bismuth solution gives the following reactions:

1. *Ammonium hydrate* precipitates white bismuth oxyhydrate $BiOOH$, which is insoluble in excess, but soluble in warm hydrochloric or nitric acid.

2. *Sodium hydrate* gives the same reaction as ammonium hydrate.

3. *Ammonium carbonate* precipitates white basic bismuth carbonate $Bi_2O_2CO_3$, which is insoluble in excess of the reagent.

4. *Sodium carbonate* gives the same reaction as ammonium carbonate.

5. *Hydrogen sulphide* precipitates dark-brown bismuth sulphide Bi_2S_3, which is insoluble in cold dilute acids, and

in ammonium sulphide, but is dissolved by boiling nitric acid.

6. *Ammonium sulphide* gives the same reaction as hydrogen sulphide. In concentrate solutions these precipitates look almost black.

7. *Potassium chromate* precipitates yellow basic bismuth chromate $Bi_2O(CrO_4)_2$, which is insoluble in sodium hydrate, but readily soluble in nitric acid; hence, in solutions which contain much free acid, no precipitate is formed.

8. *Stannous chloride*, in an excess of sodium hydrate, precipitates black bismuth oxide Bi_2O_2. To get this precipitate, add sodium hydrate to a little stannous chloride until the precipitate at first formed is dissolved in excess. Then, to this solution, add a little of the bismuth solution, a drop at a time.

9. *Water*, in a large quantity, precipitates white bismuth oxynitrate $BiONO_3$ from solutions that are not too strongly acid. To perform this operation, a test tube is nearly filled with water, and 2 or 3 drops of the bismuth solution are added to it. If this solution is not too strongly acid, a precipitate will be formed almost immediately. If it does not appear in a few seconds, a little ammonium chloride should be added, when, if the solution does not contain a large amount of acid, a precipitate will form.

ANTIMONY.

32. Antimony is a hard, brittle, bluish-white metal, which easily fuses on the charcoal before the blowpipe, depositing a white volatile incrustation of antimony oxide Sb_2O_3, while dense white fumes of this oxide are given off.

Antimony is oxidized but is not dissolved by nitric acid, and hydrochloric acid scarcely attacks it at all, but it is dissolved in aqua regia. A solution for the following reactions is best made by dissolving a trifle more than a gram of the dry antimony chloride $SbCl_3$ in hydrochloric acid and water and diluting to 100 cubic centimeters. Just enough

acid should be added to dissolve the salt, and hold it in solution.

33. Reactions.—An antimony solution gives the following reactions:

1. *Ammonium hydrate* precipitates white antimonious oxyhydrate $SbOOH$, which is insoluble in excess of the reagent.

2. *Sodium hydrate* precipitates white antimonious oxyhydrate $SbOOH$, which is easily dissolved by an excess of the reagent.

3. *Ammonium carbonate* precipitates white antimonious oxyhydrate $SbOOH$, which is but slightly soluble in excess of the reagent.

4. *Sodium carbonate* gives the same reaction as ammonia.

5. *Hydrogen sulphide* precipitates orange-red antimonious sulphide Sb_2S_3, which is insoluble in cold dilute acids, but soluble in hot concentrate hydrochloric acid, sodium hydrate, or ammonium sulphide.

6. *Ammonium sulphide* precipitates orange-red antimonious sulphide Sb_2S_3, which is soluble in excess of the reagent. From this solution the antimonious sulphide is reprecipitated by hydrochloric acid.

7. *Zinc*, when placed in a strongly acid solution of antimony, precipitates the antimony as a black powder. If a piece of platinum foil is placed in the solution in contact with the zinc, the antimony will be deposited upon it, making a black stain. This precipitate is insoluble in hydrochloric acid.

8. *Water*, in large excess, precipitates white antimonious oxychloride $SbOCl$. This precipitate is obtained in the same manner as the precipitate which water gives with bismuth (see Art. **31**, 9).

ARSENIC.

34. Arsenic is a dark-gray, brittle solid, which easily volatilizes on the charcoal before the blowpipe, without fusing, yielding a white incrustation, and white fumes of

the oxide As_2O_3, which have a characteristic garlic odor. Care must be taken not to inhale large quantities of these fumes, as they are poisonous.

Arsenic is not readily dissolved by any single acid, but aqua regia dissolves it easily, forming arsenic acid. It forms two oxides, As_2O_3 and As_2O_5, which are *acid*, while oxides of the metals are *basic*. There are two series of compounds: arsenites, which are arsen*ious* compounds; and arsenates, which are arsen*ic* compounds.

ARSENIOUS COMPOUNDS.

35. A solution of sodium arsenite is the best for the general reactions. It is made by dissolving about 1 gram of sodium arsenite Na_2HAsO_3 in 100 cubic centimeters of water.

36. Reactions.—An arsenious solution gives the following reactions:

1. *Hydrogen sulphide* gives no precipitate if the solution is neutral, but generally gives the solution a yellow color. If a little hydrochloric acid is now added, a yellow precipitate of arsenious sulphide As_2S_3 is at once formed, which is soluble in ammonia, ammonium sulphide, or ammonium carbonate, but is insoluble in hydrochloric acid, even when concentrate.

2. *Ammonium sulphide* gives no precipitate in neutral or alkaline solutions, but if a little hydrochloric acid is added to the solution, yellow arsenious sulphide As_2S_3 is formed, which is readily soluble in excess of $(NH_4)_2S$, or in ammonia, but is insoluble in hydrochloric acid.

3. *Silver nitrate* gives a slight, almost white precipitate in neutral solutions, but, if a little ammonia is added, light-yellow silver arsenite Ag_3AsO_3 is formed. A little more ammonia dissolves the precipitate, as will also nitric acid.

4. *Copper sulphate* precipitates green copper arsenite $CuHAsO_3$, which is soluble in acids and in ammonia.

5. *Copper*, when placed in an arsenious solution to which considerable hydrochloric acid has been added, becomes coated with a gray film of copper arsenide Cu_3As_2 upon boiling.

ARSENIC SOLUTIONS.

37. A good solution for the arsenic reactions is made by dissolving about 1 gram of sodium arsenate Na_2HAsO_4 in 100 cubic centimeters of water.

38. Reactions.—An arsenic solution gives the following reactions:

1. *Hydrogen sulphide* gives no precipitate with neutral solutions, but if considerable hydrochloric acid is added, the hydrogen sulphide slowly reduces the arsenic solution to arsenious, and yellow arsenious sulphide As_2S_3 is formed. This reaction is greatly helped by heating the solution. If the hydrogen-sulphide solution is very weak, it reduces the solution slowly, so that the reaction only takes place after some time, or may even fail entirely; but when a current of hydrogen-sulphide gas is led through the solution, the reaction takes place immediately. The As_2S_3 is soluble in ammonia and ammonium sulphide; but a little free sulphur, thrown out* during the reduction, usually remains in the solution, giving it a milky appearance. From this solution As_2S_3 is reprecipitated by hydrochloric acid.

2. *Ammonium sulphide* gives no precipitate with neutral solutions, but if sufficient hydrochloric acid is added, a yellow precipitate of arsenic sulphide As_2S_5 is formed.

3. *Silver nitrate*, when added to neutral arsenate solutions, produces a characteristic reddish-brown precipitate of silver arsenate Ag_3AsO_4, which is soluble in nitric acid and in ammonia.

4. *Magnesium sulphate*, under proper conditions, precipitates white crystalline, magnesium-ammonium arsenate $MgNH_4AsO_4, 6H_2O$, which is soluble in nitric acid. To get

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* The term "thrown out" means that an element is liberated from its compounds, and remains undissolved in a solution.

this precipitate, a little magnesium-sulphate solution is placed in a test tube, and precipitated with an excess of ammonia. Just enough ammonium chloride is added to dissolve the precipitate thus formed, and a little of this solution is added to a little arsenate solution in another test tube. If the solutions are dilute, the precipitate forms slowly, but is hastened by vigorous shaking.

TIN.

39. Tin is a soft, white, malleable metal that fuses easily on the charcoal before the blowpipe, forming a metallic globule and a slight, white incrustation. It is not readily dissolved in the acids separately, but is dissolved in aqua regia, forming a mixture of stannous and stannic chlorides. Hot concentrate hydrochloric acid slowly dissolves it to a solution of stannous chloride $SnCl_2$.

STANNOUS COMPOUNDS.

40. A solution for the stannous reactions is conveniently made by adding 5 cubic centimeters of concentrate hydrochloric acid and 15 cubic centimeters of water to $1\frac{1}{2}$ grams of stannous chloride and heating till it dissolves. If the solution appears milky after heating, add 5 cubic centimeters of hydrochloric acid and heat again, when it will clear up. Dilute this solution to 100 cubic centimeters with water.

41. Reactions.—A stannous solution will give the following reactions:

1. *Ammonium hydrate* precipitates white stannous hydrate $Sn(OH)_2$, which is insoluble in excess of the reagent.
2. *Sodium hydrate* precipitates white stannous hydrate $Sn(OH)_2$, which is soluble in excess of the reagent.
3. *Ammonium carbonate* precipitates white stannous hydrate $Sn(OH)_2$, which is insoluble in excess of the reagent.
4. *Sodium carbonate* gives the same reaction as ammonium carbonate.

5. *Hydrogen sulphide*, when added to solutions containing much free acid, at first colors the liquid brown, but if more is added, a brown precipitate of stannous sulphide SnS is formed. If but little free acid is present, the brown precipitate is formed at once.

6. *Ammonium sulphide* precipitates brown stannous sulphide SnS. The brown stannous sulphide precipitated by hydrogen or ammonium sulphide is soluble in yellow ammonium sulphide. Hydrochloric acid precipitates yellow stannic sulphide SnS_2 from this solution. Yellow ammonium sulphide is made by adding sulphur, in the form of powder, to common ammonium sulphide and shaking till it is dissolved. It is a polysulphide of varying composition.

42. Stannous chloride acts as a reducing agent; that is, it tends to change reducible compounds to a lower state of oxidation, while it is changed to a stannic compound. Its reaction with mercuric compounds (Art. **25**, 8) is a good example of this.

STANNIC COMPOUNDS.

43. A solution of stannic chloride $SnCl_4$ may be used for the stannic reactions. It is prepared by dissolving about $1\frac{1}{2}$ grams of stannous chloride in 5 cubic centimeters of concentrate hydrochloric acid and 15 cubic centimeters of water. Heat this to boiling and add potassium chlorate, a little at a time, until the solution becomes distinctly yellow. Then boil till the solution becomes clear, and the potassium chlorate will have oxidized the stannous to stannic chloride. After diluting to 100 cubic centimeters the solution is ready for use.

44. Reactions.—A stannic solution gives the following reactions:

1. *Ammonium hydrate* precipitates white stannic oxyhydrate, generally called metastannic acid $SnO(OH)_2$, which is insoluble in excess of the reagent.

2. *Sodium hydrate* precipitates white stannic oxyhydrate $SnO(OH)_2$, which is soluble in excess of the reagent and in acids.

3. *Ammonium carbonate* precipitates white stannic oxyhydrate $SnO(OH)_2$, which is insoluble in excess of the reagent, but soluble in acids.

4. *Sodium carbonate* gives the same reaction as ammonium carbonate.

5. *Hydrogen sulphide* precipitates light-yellow stannic sulphide SnS_2, which is soluble in hot concentrate hydrochloric acid and in ammonium sulphide. From the solution in ammonium sulphide, it is reprecipitated by hydrochloric acid.

6. *Ammonium sulphide* precipitates yellow stannic sulphide SnS_2, which is easily dissolved by an excess of the reagent. Hydrochloric acid reprecipitates it from this solution.

7 *Zinc* precipitates all the tin from both stannous and stannic solutions that contain an excess of hydrochloric acid, in the form of a dark-gray powder.

45. All compounds of tin, when mixed with sodium carbonate and placed on the charcoal before the blowpipe, are easily reduced to a bright metallic globule.

IRON.

46. Iron is a gray, hard, tenacious metal that is only fused at very high temperatures. It corrodes quite readily in the air, forming oxides. It forms two series of compounds, known as ferrous and ferric. It is easily dissolved by hydrochloric, sulphuric, or nitric acid.

FERROUS COMPOUNDS.

47. For the reactions, a solution of ferrous sulphate is the best. It is made by dissolving about 2 grams of the crystals in 100 cubic centimeters of water to which half a

cubic centimeter of concentrate sulphuric acid is added. This solution should be used when fresh, as all ferrous solutions are oxidized to ferric in the air.

48. Reactions.—A ferrous solution gives the following reactions:

1. *Ammonium hydrate* precipitates green ferrous hydrate $Fe(OH)_2$. Upon standing in the air for some time, this is partially oxidized and assumes a reddish-brown color.

2. *Sodium hydrate* precipitates light-green ferrous hydrate $Fe(OH)_2$, which is insoluble in excess. On standing in the air, its color changes to dark green and finally to reddish brown, owing to oxidation to ferric hydrate $Fe(OH)_3$ by the oxygen of the air.

3. *Ammonium carbonate* precipitates white ferrous carbonate $FeCO_3$, which almost immediately assumes a green color, and upon standing in the air becomes a reddish brown, owing to the formation of ferric hydrate.

4. *Sodium carbonate* gives the same reaction as ammonium carbonate.

5. *Hydrogen sulphide* does not precipitate iron or any of the following metals from acid solutions. Ferric solutions frequently, and some of the others more rarely, throw out free sulphur, giving the solution a milky appearance.

6. *Ammonium sulphide* precipitates black ferrous sulphide FeS, easily dissolved by hydrochloric or sulphuric acid.

7. *Potassium ferrocyanide* precipitates blue potassium ferrous ferrocyanide $K_2Fe_2''(CN)_6$.

8. *Potassium ferricyanide* precipitates deep-blue ferrous ferricyanide $Fe_3''Fe_2'''(CN)_{12}$, which is insoluble in dilute acids.

FERRIC SOLUTIONS.

49. Ferric solutions may be obtained by dissolving metallic iron in nitric acid, by oxidizing a ferrous salt by means of an oxidizing agent, such as nitric acid or potassium chlorate, or by dissolving a ferric salt, such as ferric chloride, in water, with the addition of a few drops of acid. A good

way to prepare a solution for the reactions is to dissolve about 1½ grams of ferrous sulphate crystals in from 25 to 50 cubic centimeters of water, and heat to boiling. To this boiling solution add a few drops of concentrate nitric acid, and continue the boiling till the solution becomes a clear yellow, adding a few more drops of nitric acid, if necessary, to produce this change. The nitric acid completely oxidizes the iron in hot solutions.

50. Reactions.—A ferric solution gives the following reactions:

1. *Ammonium hydrate* precipitates reddish-brown ferric hydrate $Fe(OH)_3$, which is insoluble in excess of the reagent, but soluble in acids.
2. *Sodium hydrate* gives the same reaction as ammonium hydrate.
3. *Ammonium carbonate* precipitates reddish-brown ferric hydrate $Fe(OH)_3$, and CO_2 is set free. The precipitation is aided by boiling.
4. *Sodium carbonate* gives the same reaction as ammonium carbonate.
5. *Ammonium sulphide* reduces ferric compounds to ferrous, and precipitates black ferrous sulphide FeS. Hydrochloric acid dissolves this readily, leaving the free sulphur, thrown out during reduction, in the solution.
6. *Potassium ferrocyanide* precipitates dark-blue ferric ferrocyanide $Fe_4'''Fe_3''(CN)_{18}$, which is insoluble in dilute acids.
7. *Potassium sulphocyanide* imparts a deep-red color to ferric solutions, due to the formation of soluble ferric sulphocyanide $Fe(SCN)_3$. This reaction is very delicate, mere traces of a ferric compound giving a distinct color.

ALUMINUM.

51. Aluminum, or aluminium, is a white, very light, malleable metal, that is scarcely acted on by nitric or sulphuric acid, but is quite easily dissolved in hydrochloric acid.

It is only fused at very high temperatures, and is very hard to reduce from its compounds. Its valence is always III. A solution for its reactions may be made by dissolving about 2½ or 3 grams of pure alum $AlK_2(SO_4)_2, 12H_2O$ in 100 cubic centimeters of water and a drop or two of concentrate sulphuric acid.

52. Reactions.—An aluminum solution gives the following reactions:

1. *Ammonium hydrate* precipitates white aluminum hydrate $Al(OH)_3$, which is insoluble in an excess of the reagent, but is easily dissolved by acids.
2. *Sodium hydrate* precipitates white aluminum hydrate $Al(OH)_3$, which is soluble in an excess of the reagent. From this solution aluminum hydrate is reprecipitated by ammonium chloride, especially when boiled, but hydrogen sulphide does not produce a precipitate in this solution.
3. *Ammonium carbonate* precipitates white aluminum hydrate $Al(OH)_3$, which is insoluble in an excess of the precipitant, but is readily dissolved by acids.
4. *Sodium carbonate* precipitates white aluminum hydrate $Al(OH)_3$, which is very slightly soluble in an excess of the reagent.
5. *Ammonium sulphide* precipitates white *aluminum hydrate*. To see this precipitate well, care must be taken. A small quantity of the solution is placed in a test tube, and a few drops of the reagent are added, allowing it to run down the side of the inclined tube so that it will not mix with the solution, but remain as a separate layer on the top. The precipitate appears where the two liquids meet.
6. *Sodium phosphate* precipitates white aluminum phosphate $AlPO_4$, which is insoluble in acetic acid.

CHROMIUM.

53. Chromium is a hard, heavy metal, with a strong affinity for oxygen. When acting as a base, it appears to be trivalent, but it takes more oxygen, forming an acid radical.

A solution for the reactions may be made by dissolving about 2 grams of chrome alum $CrK(SO_4)_2, 12H_2O$ in 100 cubic centimeters of water to which a drop or two of sulphuric acid is added.

54. Reactions.—A solution of chromium gives the following reactions:

1. *Ammonium hydrate* precipitates greenish-blue chromium hydrate $Cr(OH)_3$, which is slightly soluble in excess of the reagent. The part that dissolves gives the solution a reddish color. It may be reprecipitated by boiling off the excess of ammonia.
2. *Sodium hydrate* precipitates greenish-blue chromium hydrate $Cr(OH)_3$, which is soluble in excess of the reagent. It may be reprecipitated from this solution by ammonium chloride.
3. *Ammonium carbonate* precipitates greenish-blue basic chromium carbonate of varying composition.
4. *Sodium carbonate* gives the same reaction as ammonium carbonate.
5. *Ammonium sulphide* precipitates greenish-blue *chromium hydrate* $Cr(OH)_3$, which is very slightly soluble in an excess of the reagent.

55. *Chromium compounds* impart a yellowish-green color to the borax bead when hot, which changes to an emerald green upon cooling. To get this bead, heat the loop of the platinum wire and quickly dip it into borax, which will cling to the heated wire. This is then heated in the hottest part of the flame of a Bunsen burner, or in the blowpipe flame, until it is thoroughly fused and looks like a glass bead. It is now touched to a very small piece of a chromium compound, which will adhere to the soft, hot bead, and is again placed in the hottest part of the flame of the burner or the blowpipe until it is thoroughly fused. If the proper amount of the substance was taken, the bead will now assume the green color. The student must learn from experience the proper amount to take, but should guard against taking too large a quantity.

A little of one of the chromium precipitates may be tested

on the bead in this way, or enough of a rather strong chromium solution will adhere to the bead, especially if the bead is dipped into it several times, to give it a good color.

56. All chromium compounds, when fused on the platinum foil with sodium carbonate and potassium nitrate, are oxidized to chromates. To perform this operation, bend the platinum foil into the form of a spoon and place upon it about 1 cubic centimeter of dry sodium carbonate, and a little more than half as much potassium nitrate. To this add a piece of the wet chromium precipitate about half as large as a pea, or a much smaller piece of the dry compound. By means of the forceps, hold this in the hottest part of the Bunsen flame till it is thoroughly fused. When cool, place in a small beaker, or other convenient vessel, and dissolve off the fusion in equal parts of water and acetic acid, using only such a quantity as is necessary to dissolve it, and boil till all carbon dioxide is driven off. The chromium exists in the solution as an alkaline chromate, and gives the solution a slight yellow color. From this solution, lead acetate precipitates yellow lead chromate, which is easily soluble in sodium hydrate.

COBALT.

57. Cobalt is a steel-gray, rather hard, malleable metal, that is only fused at very high temperatures. It is slowly dissolved in hydrochloric or sulphuric acid, but dissolves readily in nitric acid. The solutions and crystalline salts are red, but the anhydrous salts are blue. A solution of the nitrate is best used for the reactions. It may be made by dissolving about 2 grams of the crystals, $Co(NO_3)_2, 6H_2O$, in 100 cubic centimeters of water and adding a drop or two of nitric acid.

58. Reactions.—A cobalt solution gives the following reactions:

1. *Ammonium hydrate* precipitates a blue basic cobalt compound, which easily dissolves in excess of reagent to a

brown solution. The presence of much free acid, or of ammonium salts, prevents the precipitation.

2. *Sodium hydrate* precipitates a blue basic compound which is insoluble in excess. If the precipitate in the excess of reagent be boiled, it changes to a pale-red precipitate of cobaltous hydrate $Co(OH)_2$. This soon changes to brown, owing to the formation of cobaltic oxide Co_2O_3.

3. *Ammonium carbonate* precipitates a reddish basic cobalt carbonate, which is soluble in excess of the reagent, forming a red solution.

4. *Sodium carbonate* precipitates a reddish basic cobalt carbonate, which is insoluble in an excess of the reagent.

5. *Ammonium sulphide* precipitates black cobalt sulphide CoS, which is but very slightly soluble in hydrochloric acid, especially if it has been precipitated at a boiling temperature, but is dissolved by hot nitric acid.

6. *Potassium nitrite* gives a yellow precipitate, which is probably potassium cobaltic nitrite, from acetic-acid solutions. To get this precipitate, add ammonia to the solution till a slight precipitate is formed. Dissolve this in a slight but distinct excess of acetic acid, and to this solution add a stick of the dry potassium nitrite from 1 to 2 inches long, and stand aside for some time in a rather warm place. The cobalt is completely precipitated from a strong solution in a short time, and somewhat more slowly from a dilute one.

This is an important reaction, as it serves to separate cobalt and nickel, the cobalt being all precipitated, while the nickel remains in solution. Fresenius gives the probable composition of the precipitate as $2K_3Co(NO_2)_6, 3H_2O$.

59. Compounds of cobalt impart a deep-blue characteristic color to the borax bead, made as described under "Chromium," Art. **55.**

NICKEL.

60. Nickel is a bright, hard, malleable metal with a yellowish-white color. It is very hard to fuse, and is not oxidized in the air at ordinary temperature, but slowly

oxidizes when ignited. It is slowly dissolved in hydrochloric or sulphuric acid, and very readily in nitric acid.

A solution of the nitrate may be used for the reactions. It is made by dissolving about 2 grams of the crystals $Ni(NO_3)_2, 6H_2O$ in 100 cubic centimeters of water, and adding a drop or two of nitric acid.

61. Reactions.—A nickel solution gives the following reactions:

1. *Ammonium hydrate* gives a slight greenish precipitate, which is very soluble in excess to a deep-blue solution. If ammonium salts are present, or if the solution contains much free acid, no precipitate is formed, but the blue solution appears at once.

2. *Sodium hydrate* precipitates green nickel hydrate $Ni(OH)_2$, which is insoluble in excess of the reagent, but is soluble in ammonium chloride.

3. *Ammonium carbonate* precipitates light-green basic nickel carbonate, which is soluble in excess of the reagent.

4. *Sodium carbonate* precipitates light-green basic nickel carbonate of variable composition, which is insoluble in excess of the reagent.

5. *Ammonium sulphide* precipitates black nickel sulphide NiS, which is but slightly soluble in cold dilute hydrochloric acid, but is readily dissolved by warm nitric acid.

ZINC.

62. Zinc is a bluish-white metal that tarnishes in the air, owing to the formation of a thin coat of basic zinc carbonate. It is rather brittle and is fusible. On the charcoal before the blowpipe, it fuses and deposits an incrustation of zinc oxide ZnO, which is yellow when hot and white when cold.

Chemically pure zinc is only slowly attacked by hydrochloric or sulphuric acid, but is dissolved in nitric acid. Common zinc, which contains small quantities of other

metals, dissolves readily in hydrochloric or sulphuric acid, and is largely used in the laboratory for the preparation of hydrogen, which is accomplished by dissolving zinc in one of these acids.

A solution for the zinc reactions is conveniently prepared by dissolving about 2 or 2½ grams of zinc sulphate $ZnSO_4, 7H_2O$ in 100 cubic centimeters of water to which is added a drop of dilute sulphuric acid.

63. Reactions.—A zinc solution gives the following reactions:

1. *Ammonium hydrate* precipitates white zinc hydrate $Zn(OH)_2$, which is easily soluble in excess of the reagent. From solutions containing much free acid or ammonium salts the zinc is not precipitated by ammonia.

2. *Sodium hydrate* precipitates white zinc hydrate $Zn(OH)_2$, which is soluble in excess of the reagent. From this solution the zinc is not reprecipitated by ammonium chloride, but is reprecipitated by hydrogen sulphide.

3. *Ammonium carbonate* precipitates white basic zinc carbonate, which is soluble in excess of the reagent.

4. *Sodium carbonate* precipitates white basic zinc carbonate, which is only slightly soluble in excess.

5. *Ammonium sulphide* precipitates white zinc sulphide ZnS, which is insoluble in excess, but easily soluble in hydrochloric, sulphuric, and nitric acids. The precipitation is hastened by the presence of ammonium chloride, and also by warming.

6. *Potassium ferrocyanide* precipitates white zinc ferrocyanide $Zn_2Fe(CN)_6$, which is insoluble both in acids and in ammonia.

MANGANESE.

64. Manganese is a dull-gray, very hard, brittle metal. It only fuses at very high temperatures. It is rapidly oxidized in moist air or water, and is readily dissolved by acids.

A solution of manganese sulphate may be used for the

reactions. It is prepared by dissolving from 2 to 3 grams of the crystals, $MnSO_4, 7H_2O$, in 100 cubic centimeters of water, and adding a drop or two of dilute sulphuric acid.

65. Reactions.—A manganese solution gives the following reactions:

1. *Ammonium hydrate* precipitates white manganese hydrate $Mn(OH)_2$ from solutions that do not contain much free acid or ammonium salts. This rapidly changes to brown $MnOOH$. If much ammonium chloride is present, it prevents the immediate precipitation of the manganese, but after oxidizing it sometimes separates slowly from the solution.

2. *Sodium hydrate* precipitates white manganese hydrate $Mn(OH)_2$, which is insoluble in excess, but slightly soluble in ammonium chloride. Upon exposure to air the white precipitate changes to brown, owing to the oxidation of the manganese to $MnOOH$.

3. *Ammonium carbonate* precipitates white manganese carbonate $MnCO_3$ In the air this precipitate slowly changes to brown.

4. *Sodium carbonate* precipitates white manganese carbonate $MnCO_3$, which is insoluble in excess of the reagent, but when freshly precipitated is soluble in ammonium chloride.

5. *Ammonium sulphide* precipitates flesh-colored manganese sulphide MnS, which is easily dissolved by acids.

6. If, to about half a cubic centimeter of lead dioxide in a test tube, we add a few drops of manganese solution, and then about 8 cubic centimeters of an acid made by mixing equal volumes of concentrate nitric acid and water, and boil the whole for about two minutes, permanganic acid $HMnO_4$ is formed, which gives the liquid a distinct red color. This may be seen as soon as the black insoluble matter has settled to the bottom.

66. Manganese compounds impart an amethyst-red color to the borax bead, when heated in the oxidizing flame. This

must be done as described under "Chromium," Art. **55.** If this bead be reheated for some time in the reducing flame, it loses its color, on account of the reduction of the manganese to a colorless compound.

67. Compounds of manganese, when fused on platinum foil with sodium carbonate and potassium nitrate, are oxidized to manganates, and give a dark-green color to the fusion. This should be done as described under "Chromium," Art. **56.**

BARIUM.

68. Barium compounds cannot be reduced on the charcoal before the blowpipe, but when heated very high these compounds become incandescent.

A good solution for the barium reactions is made by dissolving about 2 grams of barium chloride $BaCl_2$ in 100 cubic centimeters of water and adding a drop or two of dilute hydrochloric acid.

69. Reactions.—A barium solution gives the following reactions:

1. *Ammonium hydrate* does not give a precipitate with barium, strontium, or calcium solutions.

2. *Sodium hydrate* does not give a precipitate from ordinary barium solutions, but precipitates white barium hydrate $Ba(OH)_2$ from very strong solutions.

3. *Ammonium carbonate* precipitates white barium carbonate $BaCO_3$, which is insoluble in ammonium chloride, but soluble in hydrochloric acid. Heat aids the precipitation.

4. *Sodium carbonate* precipitates white barium carbonate $BaCO_3$, which dissolves in hydrochloric acid with effervescence.

5. *Ammonium sulphide* does not precipitate this or any of the following metals.

6. *Potassium chromate* precipitates yellow barium chromate, which is easily soluble in hydrochloric acid, but is insoluble in sodium hydrate or acetic acid. From the hydrochloric-acid solution it is reprecipitated by ammonia.

7. *Sulphuric acid* precipitates white barium sulphate $BaSO_4$. The precipitate is formed immediately, and is almost insoluble in all acids. A soluble sulphate may be used instead of sulphuric acid, and the same result obtained. Calcium sulphate precipitates barium sulphate from barium solutions immediately.

8. *Ammonium oxalate* gives no precipitate in dilute solutions, but in rather strong solutions it precipitates white barium oxalate BaC_2O_4, which is easily soluble in nitric, hydrochloric, or acetic acid.

9. *Sodium phosphate* precipitates white hydrogen barium phosphate $HBaPO_4$ from neutral and alkaline solutions. The precipitate is very soluble in hydrochloric, nitric, or acetic acid, so that in a solution containing free acid, no precipitate is formed. Such a solution may have the acid neutralized by ammonia, after which it may be precipitated by the phosphate.

70. All volatile barium compounds, as, for example, the chloride, when brought into the flame, either in the solid or liquid state, on the loop of a platinum wire, impart a characteristic yellowish-green color to the flame.

STRONTIUM.

71. Strontium is a brass-yellow metal, but is seldom seen in the metallic form, owing to its great affinity for oxygen. Its compounds can only be reduced to the oxide before the blowpipe. At a high temperature this is luminous.

A solution for the wet reactions may be made by dissolving about 2 grams of strontium nitrate in 100 cubic centimeters of water to which a drop of nitric acid has been added.

72. Reactions.—A strontium solution gives the following reactions:

1. *Sodium hydrate* precipitates, from moderately strong solutions, white strontium hydrate $Sr(OH)_2$, which is dissolved by adding water and boiling. In very dilute solutions no precipitate is formed.

2. *Ammonium carbonate* precipitates white strontium carbonate $SrCO_3$, which is only very slightly soluble in ammonium chloride, but is soluble in hydrochloric, nitric, or acetic acid. Warming aids in the precipitation.

3. *Sodium carbonate* gives the same precipitate as ammonium carbonate.

4. *Potassium chromate* precipitates yellow strontium chromate $SrCrO_4$ from rather strong neutral solutions. This is easily dissolved by hydrochloric, nitric, or acetic acid, or by a large amount of water, so that in dilute solutions, or those containing much free acid, no precipitate is formed.

5. *Sulphuric acid* precipitates white strontium sulphate $SrSO_4$, which is very slightly soluble in water, so that in very dilute solutions the precipitate does not appear immediately. A saturated solution of calcium sulphate may be used instead of sulphuric acid, in which case the precipitate will appear after a few moments.

6. *Sodium phosphate* precipitates white hydrogen-strontium phosphate $HSrPO_4$ from neutral, and strontium phosphate $Sr_3(PO_4)_2$ from alkaline, strontium solutions. Both are soluble in acids, so that in strongly acid solutions no precipitate is formed.

7. *Ammonium oxalate* precipitates white strontium oxalate SrC_2O_4, which is easily soluble in hydrochloric or nitric acid, but only slightly soluble in acetic acid.

73. Strontium compounds that are volatile give a crimson color to the flame, when held in it on the loop of a platinum wire. The chloride is the most volatile of the ordinary strontium compounds, so it is well to dip the substance into hydrochloric acid just before placing it in the flame.

CALCIUM.

74. Calcium is a yellow metal, but on account of its great affinity for oxygen it is rare in the metallic state. Its compounds can only be reduced to the oxide on the charcoal

before the blowpipe. This is infusible, and luminous at high temperatures, giving what is known as the calcium light.

A solution for the wet reactions may be prepared by dissolving about 2 grams of dry calcium chloride in 100 cubic centimeters of water and adding a drop or two of hydrochloric acid.

75. Reactions.—A calcium solution gives the following reactions:

1. *Sodium hydrate* precipitates white calcium hydrate $Ca(OH)_2$, which is slightly soluble in water. Hence, in *very* dilute solutions no precipitate is formed.

2. *Ammonium carbonate* precipitates white calcium carbonate $CaCO_3$. Heat aids the precipitation. The precipitate is soluble in acids with effervescence.

3. *Sodium carbonate* precipitates white calcium carbonate $CaCO_3$, which is easily dissolved by dilute acids.

4. *Potassium chromate* gives no precipitate with calcium compounds.

5. *Sulphuric acid* precipitates white calcium sulphate $CaSO_4$ from concentrate solutions. As this is quite soluble in water, unless the solution is very strong, the precipitate forms slowly, and if the solution is dilute, no precipitate is formed. Of course, calcium sulphate would not precipitate calcium from its solutions.

6. *Ammonium oxalate* precipitates white calcium oxalate CaC_2O_4, which is insoluble in acetic acid, but easily soluble in hydrochloric or nitric acid. The presence of free ammonia and heating both favor the formation of this precipitate.

7. *Sodium phosphate* gives a white precipitate. If the solution is slightly acid or neutral, this precipitate is $HCaPO_4$, but if the solution is alkaline, the precipitate is $Ca_3(PO_4)_2$. It is easily dissolved by dilute acids, and is reprecipitated by ammonia.

76. All volatile calcium compounds, when held in the Bunsen flame on the platinum wire, impart a brick-red color to the flame. It is well to dip the substance in hydrochloric

acid just before placing it in the flame, in order to form volatile calcium chloride. If the calcium gives a very strong color to the flame it may be mistaken for strontium, but we may distinguish between them by looking at the flame through a blue glass, when the strontium flame appears purple, or rose color, while the calcium flame only shows a faint greenish-gray color.

MAGNESIUM.

77. Magnesium is a white metal that tarnishes very slowly in dry air, but much more rapidly if the air is moist. It burns in the air, with a dazzling white light, to magnesium oxide MgO

A solution of magnesium sulphate may be used for the wet reactions. It is made by dissolving about 3 grams of the crystals $MgSO_4, 7H_2O$ in 100 cubic centimeters of water and adding a drop or two of sulphuric acid.

78. Reactions.—A magnesium solution gives the following reactions:

1. *Ammonium hydrate* precipitates white magnesium hydrate $Mg(OH)_2$ from neutral solutions that are free from ammonium salts. If the solution contains any considerable amount of free acid or ammonium salts, no precipitate is formed.

2. *Sodium hydrate* precipitates white magnesium hydrate $Mg(OH)_2$ from solutions that do not contain ammonium salts. The precipitate is soluble in acids and in ammonium chloride. From the solution in ammonium chloride the magnesium hydrate may be slowly reprecipitated by continued boiling.

3. *Ammonium carbonate* gives no precipitate under ordinary conditions.

4. *Sodium carbonate* precipitates white basic magnesium carbonate from solutions that do not contain ammonium salts. Heat aids the formation of the precipitate. It is

soluble in ammonium chloride, and is prevented from forming by the presence of ammonium salts.

5. *Sodium phosphate* gives no precipitate in acid solutions, but in alkaline solutions the magnesium is completely precipitated as white magnesium-ammonium phosphate $MgNH_4PO_4$, which is easily dissolved by acids, and is reprecipitated from this solution by ammonium hydrate.

79. Magnesium compounds, when highly heated on the charcoal before the blowpipe, are reduced to the white infusible oxide, which is luminous at high temperatures. If this is moistened with a drop of cobalt nitrate, and again ignited, it assumes a pale-rose color, which is permanent, and may be seen after cooling.

AMMONIUM.

80. The ammonium group NH_4 acts like a metal, forming the base of all ammonium compounds, and is, consequently, treated as a metal. When heated on the charcoal or platinum foil, all ammonium compounds are either decomposed or volatilized, those that are decomposed giving the peculiar odor of ammonia.

A solution for its reactions may be made by dissolving 2 or 3 grams of ammonium nitrate, or chloride, in 100 cubic centimeters of water.

81. Reactions.—Ammonium compounds give the following reactions:

1. *Acid sodium tartrate* precipitates white acid ammonium tartrate $HNH_4C_4H_4O_6$ from rather concentrate solutions. It is very soluble in acids, and quite soluble in water, so that in dilute solutions, or in those containing free acid, no precipitate is formed. The precipitate is not formed at once except in very strong solutions, but shaking favors its formation. It is sometimes obtained from the solution prepared as described above, but often fails.

2. *Platinum chloride* precipitates yellow ammonium-platinum chloride $(NH_4)_2PtCl_6$ from concentrate solutions.

This precipitate is insoluble in alcohol, but is dissolved by water; hence, in dilute solutions no precipitate is formed.

Probably no precipitate can be obtained from the solution described above, but the reaction is mentioned here as it is important in later work.

3. *Sodium hydrate*, when heated with any ammonium compound, decomposes it, setting free NH_3. This is by far the best common test for ammonium, and, in fact, the only sure one. To apply this test, place a little of the solution to be tested in a test tube, add about an equal quantity of sodium hydrate, and heat. Ammonia gas is set free, which is recognized by its characteristic odor. If a piece of red litmus paper is moistened and held at the mouth of the tube, it is turned blue; or, if a drop of hydrochloric acid on a glass rod is held at the mouth of the tube where the gas comes in contact with it, white fumes of ammonium chloride NH_4Cl are formed.

POTASSIUM.

82. Potassium is a soft, silver-white metal when freshly cut, but tarnishes rapidly in air. It decomposes water, forming potassium hydrate KOH and setting free hydrogen, during which reaction heat enough is generated to ignite the hydrogen, which burns with a violet flame.

A solution for the reactions may be made by dissolving about 3 grams of potassium nitrate or chloride in 100 cubic centimeters of water.

83. Reactions.—A potassium solution gives the following reactions:

1. *Acid sodium tartrate* precipitates white acid potassium tartrate $KHC_4H_4O_6$ from neutral solutions that are not too dilute. It is easily soluble in acids and alkalies, and less so in water, so we cannot place a great deal of dependence upon it. Its formation is favored by shaking.

2. *Platinum chloride* precipitates yellow potassium-platinum chloride K_2PtCl_6 from concentrate solutions. It is insoluble in alcohol, but soluble in acids, alkalies, or water;

consequently, with the ordinary solution we may succeed or fail in getting it.

84. Potassium compounds, when brought into a colorless flame on a platinum wire, impart a bluish-violet color to the flame. This is by far the best method of recognizing potassium. Sodium and other impurities may partially obscure this color, but when viewed through the blue glass, their colors are absorbed and the potassium flame appears a reddish-violet color. After a little practice this flame may be identified with absolute certainty.

SODIUM.

85. Sodium is a soft, white metal that behaves much like potassium, except that it produces no precipitates with ordinary reagents. A solution may be made by dissolving 2 or 3 grams of sodium nitrate or chloride in 100 cubic centimeters of water.

86. As sodium gives no precipitates with ordinary reagents, we depend upon the flame to enable us to recognize it. This is easily done, as even small amounts of it impart an intense yellow color to the flame, which is not obscured by the presence of other elements. When viewed through a blue glass, the yellow color is absorbed and the flame appears almost colorless.

87. A crystal of potassium bichromate, when held close to the sodium flame, appears transparent and almost colorless in its light.

EXPLANATION OF TABLE 1.

88. If the student has performed and studied each of the reactions described under the different metals, he is now prepared to determine any single common metal in a solution, by means of these reactions. All the reactions necessary to determine any of these metals have been described, but the student will find that at first it is difficult to remember the reactions, and much time would be lost in looking

through this whole section for a metal whose reactions agree with those obtained when working with an unknown solution. Table 1 is intended to aid the student in quickly finding the metal that gives the reactions obtained with the unknown solution. It is not the purpose of this table to take the place of the description of the reactions, but to give as much as possible of the matter contained in this part of the work in tabulated form, so that the student may at once get a general view of some of the leading facts in regard to this part of the work. The method of using the table is simple. Take a little of a solution of a metal—preferably an unknown one—in a test tube and precipitate it with a reagent. Then look in the column under this reagent for precipitates that agree with the one obtained. In this way we find that the solution contains one of a few metals, and by repeating this operation with a second reagent the number of possible metals is reduced, or perhaps the metal will be located. In this way a few reactions will serve to locate any of the common metals. The letters in the columns under the reagents and opposite the metals, show the colors of the precipitates, formed by the action of these reagents on solutions of the metals. Solubility is indicated, in some cases, where it is important. It is difficult to accomplish more than this in a table of this kind. The following list explains these letters:

B.—black.	W.—white.	D. Br.—dark brown.
Bl.—blue.	R.—red.	R. Br.—reddish brown.
Br.—brown.	Y.—yellow.	D. Bl.—dark blue.
G.—green.	F.—flesh color.	G. Bl.—greenish blue.

The plus sign (+) following a letter means that the precipitate is soluble in excess; a, following a dash (—a), means that the precipitate is soluble in, or is prevented by, ammonium chloride or other ammonium salts. Thus, W.—a. means a white precipitate that is soluble in, or is prevented by, ammonium chloride or other ammonium salts. Figures placed in the columns refer to articles in this Paper. They are used in cases of reactions that cannot be fully expressed in the table.

TABLE 1.

	H_2S.	$(NH_4)_2S$.	$NaOH$.	NH_4OH.	$(NH_4)_2CO_3$.	Na_2CO_3.	Na_2HPO_4.	HCl.	H_2SO_4.	$K_4Fe(CN)_6$.	H_2O.	$AgNO_3$.
Ag.....	B.	B.	Br.	18	W.+	W.		W.				
Pb........	B.	B.	W.+	W.	W.	W.		W.	W.			
Hg (*ous*)	B.	B.	B.	B.	W. 23	W. 23		W.	W.			
Hg (*ic*)...	B.	B.	Y.	W.	W.	R. Br.						
Cu.....	B.	B.	Bl.	Bl.+ 27	Bl.+	Bl.				R. Br.		
Cd.....	Y.	Y.	W.	29	W.+	W.						
Bi......	D. Br.	D. Br.	W.	W.	W.	W.					W. 31	
Sb......	R.	R.+	W.+	W.	W.	W.					W. 33	
As (*ous*)	Y. 36	Y.+										W. 36
As (*ic*)..	38	38										R. Br. 38

Sn (*ous*)	D. Br.	D. Br.+	W.+	W.	W.	W.					
Sn (*ic*)	Y.	Y.+	W.+	W.	W.	W.					
Fe (*ous*)		B.	G.	G.	G. 48	G.				Bl.	
Fe (*ic*)		B.	R. Br.	R. Br.	R. Br.	R. Br.				D. Bl.	
Al		W.	W.+	W.	W.	W.					
Cr		G. Bl.	G. Bl.+	G. Bl.	G. Bl.	G. Bl.					
Co.		B.	Bl.	Bl.+	R.+	R.					
Ni		B.	G.—a.	G.+ 61	G.+	G.					
Zn		W.	W.+	W.+	W.+	W.				W.	
Mn		F.	W.	W.—a.	W.	W.—a.					
Ba			69		W.	W.	W. 69		W.		
Sr.			W. 72		W.	W.	W. 72		W.		
Ca			W.		W.	W.	W.		W. 75		
Mg			W.—a.	W.—a.		W.—a.	W. 78				
NH_4	Odor with $NaOH$.										
K	Color of flame.										
Na	Color of flame.										

GENERAL REMARKS.

89. No scheme will be given for the determination of the metals where there is but one metal in the solution, for this should be a logical exercise; each step depending upon the preceding one. To be sure, the scheme for the separation of the metals, to be given later, may be followed, but in this case the student, by merely following directions, misses much of the benefit derived from working out a scheme for himself, as he proceeds with the determination, and besides that, he wastes much time, as in nearly every case the metal may be determined much more quickly by logically working out a scheme as he proceeds with the determination. No fixed rule can be laid down for this work, as each operation should be governed by what we learn as we proceed. For instance, if we use hydrogen sulphide as the first reagent, the reagent with which we test the second portion of the solution will depend upon what we learn from this. If we obtain a precipitate with hydrogen sulphide, it would be useless to try ammonium sulphide, for this would give us the same precipitate; but if no precipitate is obtained with hydrogen sulphide, we could not do better than to use ammonium sulphide as the second reagent, in order to learn if the metal is one of those which is not precipitated by hydrogen sulphide, but is precipitated by ammonium sulphide.

The reagent to be used first is a matter of personal preference. Some chemists prefer hydrogen sulphide, others use sodium hydrate as the first reagent, and still others—following more nearly the plan adopted for the separation of the metals—use hydrochloric acid to start the analysis. In any case the student should consider carefully what is indicated by this reagent, and the second one should be chosen with a view to reducing, as much as possible, the number of metals that may be present.

This may seem difficult at first, but after a little practice it becomes very easy, and by studying out methods of work that make each process a logical one, the student acquires that knowledge of chemical relations and that habit of thought without which he will never make any great progress in chemical science.

ANALYSIS OF MIXED SOLUTIONS.

90. We now have before us all the facts necessary to make out a scheme by which we can separate and determine several metals mixed together in a solution, but, as for this work, we need some apparatus in addition to that already in use, and as some of the operations differ from any thus far performed, we will describe these before proceeding to describe the process.

91. Apparatus Needed for Separations.—In addition to the apparatus already in use, we need a wash bottle, funnels, support for funnels, filter paper, beakers, a porcelain dish, a stirring rod, and a flask.

1. A wash bottle is made by fitting a flask with a stopper that has two perforations. Through one of these perforations a tube (*b*, Fig. 8) is passed so that the lower end just projects through the bottom of the stopper. The upper part of the tube is bent so that it forms an angle of about 60°. Through the other perforation a tube is passed, reaching nearly to the bottom of the flask. The top of this tube is bent so that it forms an angle of about 120°, and the end is drawn out, leaving a small

FIG. 8.

opening. The tubes must fit tightly into the perforations in the stopper. By blowing in the tube *b*, the pressure of the air forces the water in the flask up through the tube *a* and out of the small opening in a fine jet that is very well adapted to the purpose of washing precipitates, and of washing out small particles of substance that adhere to a beaker. The tube *a* is often cut in two, about half way between the bend and the tip, and the two parts held together by placing over them a piece of rubber tubing that fits them closely. This makes it much handier to direct the jet of water. As hot water is often used in a wash bottle, the neck of the flask is frequently covered, to protect the hand from the

heat. This may be done by wrapping it with a cord, or by binding a ring of cork around it.

2. The funnels used in all ordinary analytical work must be of glass. The ring of a retort stand serves very well for a support in filtering.

3. Filter paper may be obtained from any chemical dealer, either in sheets, or cut in disks, ready for use. The papers 4 inches in diameter (10 centimeters) are the best size for qualitative work. The filter papers are folded as directed in Art. **99**, *Theoretical Chemistry*.

4. A nest of beakers, a porcelain dish, a common glass stirring rod, and a flask require no description.

92. Washing Precipitates.—There are two methods of washing precipitates, known as *washing by decantation* and *washing on the filter*. In washing by decantation, the precipitate is allowed to settle to the bottom of the beaker and the clear liquid is poured off, or decanted; water is added, the precipitate is stirred up with it, and then is allowed to settle, and the water decanted. This may be repeated several times, the water carrying off a large part of the remaining impurity each time, until the precipitate is free from foreign matter.

In washing on the filter, the precipitate is separated from the liquid by means of filtration, as described in Art. **99**, *Theoretical Chemistry*. After all the liquid has passed through, leaving the precipitate on the filter, a jet of water from the wash bottle is directed around the top of the filter paper, thus washing down any impurity that may be absorbed by this part of the paper, and washing the precipitate down nearer the cone of the paper. When a little more than enough water to cover the precipitate has been added in this way, allow it all to run through the filter before adding more. By repeating this operation a few times, the water carries all soluble matter through the filter, leaving the precipitate clean.

93. Concentrating Filtrates, or Solutions.—In separating the different metals, we precipitate some of them

from the solution, and then get others from the filtrate. The water used in washing the precipitates, of course, goes into the filtrates and in a short time our solution becomes too large. To avoid this we must concentrate the solution, and this is always done by evaporating off some of the water. This is rapidly accomplished by boiling the liquid. Liquids in a beaker must always be heated over a wire gauze. Stand the beaker on a gauze, resting on a tripod, and place the burner under it. The flame must never be turned high enough to reach around the side of the gauze and strike the beaker, or it will probably crack it. This applies to heating liquids in any glass vessel. The same care must be taken when heating water in a wash bottle.

GROUP SEPARATIONS.

94. As has already been indicated, when there are several metals in a solution, they are removed from the solution in groups by means of the so called *group reagents*, and the metals in each group are then separated from each other. There are six of these group reagents; and, by means of them, all the common metals may be divided into seven groups. The group reagents, in the order in which they are used, are: *hydrochloric acid*, *hydrogen sulphide*, *ammonium hydrate*, *ammonium sulphide*, *ammonium carbonate*, and *sodium phosphate*. There is no group reagent for the seventh group, as it consists of the metals that are not precipitated by any of the common reagents.

Group I consists of the metals that are precipitated as chlorides by hydrochloric acid. They are:

Silver..................	white.
Lead (incompletely)....	"
Mercurous.............	"

Group II consists of the metals left in the filtrate that are precipitated as sulphides by hydrogen sulphide. On account of the solubility of lead chloride in water, some of the lead is precipitated in the second group. This group is divided

into two divisions, depending upon the solubility of the sulphides in ammonium sulphide and ammonium hydrate. The group is as follows:

Division A.		Division B.	
Insoluble in $(NH_4)_2S$ and NH_4OH.		*Soluble in $(NH_4)_2S$ and NH_4OH.*	
Lead	black.	Antimony	orange.
Mercuric	"	Stannous	brown.
Copper	"	Stannic	yellow.
Cadmium	yellow.	Arsenious	"
Bismuth	brown.	Arsenic	"

Group III consists of the remaining metals that are precipitated as hydrates by ammonium hydrate in the presence of ammonium chloride. They are:

Iron	reddish brown.
Chromium	greenish blue.
Aluminum	white.

Group IV consists of the remaining metals that are precipitated as sulphides by ammonium sulphide. They are:

Cobalt	black.
Nickel	"
Zinc	white.
Manganese	flesh color.

Group V consists of the metals not precipitated in any of the previous groups, but that are precipitated as carbonates by ammonium carbonate, in the presence of ammonium chloride. They are:

Barium	white.
Strontium	"
Calcium	"

Group VI contains but one metal. It is not precipitated by any of the preceding group reagents, but is precipitated by sodium phosphate in the presence of ammonia and ammonium chloride. It is:

Magnesium	white.

Group VII consists of the metals that are not precipitated by any of the common reagents, but must be recognized by special tests. They are:

Ammonium, Potassium, Sodium.

The rare metals are not treated here, as their treatment at this time would complicate the work too much. They are, therefore, taken up later and treated by themselves.

GROUP I.

95. About 20 cubic centimeters of the solution to be analyzed are placed in the smallest beaker and about 3 drops of concentrate hydrochloric acid added. If no precipitate is formed, this portion of the solution is ready for the next step, and should be treated for Group II. If the solution contains silver, lead, or mercurous compounds, they will be precipitated, except in the case of very small quantities of lead, which, on account of the solubility of its chloride in water, may not be precipitated in this group, but will come down in Group II. If a precipitate is formed, continue to add hydrochloric acid gradually, and with constant stirring, till all the metals of this group are precipitated, but taking care not to add a large excess of the reagent. We can tell when enough of the reagent has been added by allowing the precipitate to settle, and adding a drop or two of the reagent. The precipitation is complete when this no longer produces a precipitate in the clear liquid. Allow the precipitate to settle, and filter as directed in Art. **99**, *Theoretical Chemistry*, and wash two or three times on the filter with cold water. Receive the filtrate in the next to the smallest beaker and set it aside, to be treated for Group II. It is best before doing so, however, to add a drop or two of the reagent to the filtrate, in order to be sure that the precipitation was complete. If a precipitate is formed, it shows that the metals of this group have not been perfectly separated, and the reagent must be added till a precipitate is no longer formed. This must then be filtered and the precipitates united. This

into two divisions, depending upon the solubility of the sulphides in ammonium sulphide and ammonium hydrate. The group is as follows:

DIVISION A.		DIVISION B.	
Insoluble in $(NH_4)_2S$ and NH_4OH.		*Soluble in $(NH_4)_2S$ and NH_4OH.*	
Lead	black.	Antimony	orange.
Mercuric	"	Stannous	brown.
Copper	"	Stannic	yellow.
Cadmium	yellow.	Arsenious	"
Bismuth	brown.	Arsenic	"

Group III consists of the remaining metals that are precipitated as hydrates by ammonium hydrate in the presence of ammonium chloride. They are:

Iron..............reddish brown.
Chromium ....greenish blue.
Aluminum ....white.

Group IV consists of the remaining metals that are precipitated as sulphides by ammonium sulphide. They are:

Cobalt...............black.
Nickel............... "
Zinc.................white.
Manganese...........flesh color.

Group V consists of the metals not precipitated in any of the previous groups, but that are precipitated as carbonates by ammonium carbonate, in the presence of ammonium chloride. They are:

Barium ....white.
Strontium................ "
Calcium.................. "

Group VI contains but one metal. It is not precipitated by any of the preceding group reagents, but is precipitated by sodium phosphate in the presence of ammonia and ammonium chloride. It is:

Magnesium................white.

Group VII consists of the metals that are not precipitated by any of the common reagents, but must be recognized by special tests. They are:

Ammonium, Potassium, Sodium.

The rare metals are not treated here, as their treatment at this time would complicate the work too much. They are, therefore, taken up later and treated by themselves.

GROUP I.

95. About 20 cubic centimeters of the solution to be analyzed are placed in the smallest beaker and about 3 drops of concentrate hydrochloric acid added. If no precipitate is formed, this portion of the solution is ready for the next step, and should be treated for Group II. If the solution contains silver, lead, or mercurous compounds, they will be precipitated, except in the case of very small quantities of lead, which, on account of the solubility of its chloride in water, may not be precipitated in this group, but will come down in Group II. If a precipitate is formed, continue to add hydrochloric acid gradually, and with constant stirring, till all the metals of this group are precipitated, but taking care not to add a large excess of the reagent. We can tell when enough of the reagent has been added by allowing the precipitate to settle, and adding a drop or two of the reagent. The precipitation is complete when this no longer produces a precipitate in the clear liquid. Allow the precipitate to settle, and filter as directed in Art. **99**, *Theoretical Chemistry*, and wash two or three times on the filter with cold water. Receive the filtrate in the next to the smallest beaker and set it aside, to be treated for Group II. It is best before doing so, however, to add a drop or two of the reagent to the filtrate, in order to be sure that the precipitation was complete. If a precipitate is formed, it shows that the metals of this group have not been perfectly separated, and the reagent must be added till a precipitate is no longer formed. This must then be filtered and the precipitates united. This

applies to the succeeding groups as well as to this one, but in every case care must be taken not to add a large excess of the reagent.

Punch a hole in the apex of the filter with a stirring rod, and wash the precipitate through into the small beaker with hot water, using enough water to about half fill the beaker. Place this on the gauze and heat it to boiling while stirring it with a glass rod. If it all dissolves, there is only lead present, which should be confirmed by adding a few drops of sulphuric acid to a portion of it, and also by the other reactions for lead. If the precipitate does not all dissolve, it should be filtered while hot. The lead chloride will go through in the filtrate, and the silver and mercurous chlorides will remain on the filter. Test the filtrate for lead by adding sulphuric acid, and by means of potassium chromate, as described under "Lead," in the "Deportment of the Metals With Reagents." This may now be thrown away, the beaker washed, and placed under the funnel. Ammonium hydrate is now added to the precipitate on the filter. If silver chloride is present, it is dissolved and runs through the filter, forming a new filtrate, while the mercurous chloride is changed to a black, insoluble compound that remains on the filter. Nitric acid is added to the ammoniacal filtrate, or to a part of it, in sufficient quantity to render it slightly acid, when silver, if present, will be reprecipitated as chloride. The blackening of the precipitate on the filter, when ammonia is added, is proof of mercurous chloride; but this may be dissolved in a little aqua regia, and after evaporating the excess of acid and diluting, it may be confirmed by the use of stannous chloride, and by the other reactions for mercury.

GROUP II.

96. The first filtrate from Group I, or the slightly acid solution, if none of the members of Group I were present, is now ready to be treated for Group II. But before treating the whole of the solution with hydrogen sulphide, a small portion in a test tube should be tried to see if any of the

members of the second group are present. This may be done by adding a little of the hydrogen-sulphide solution, if proper precautions are taken to precipitate arsenic, if present. But it is best to run a little of the gas through this solution. If no precipitate is obtained in this *side test*, it is thrown out, and the main part of the filtrate is ready to treat for Group III. If a precipitate is obtained, it shows the presence of second-group metals, and the solution must be treated with hydrogen sulphide. The hydrogen-sulphide solution is too dilute for this purpose, so we must use the gas. It is prepared as described in Art. **105**, Experiment 50, *Inorganic Chemistry*, Part 1, and is led into the solution until the precipitation of the metals of Group II is complete. This will generally take about 10 minutes. After a little practice the student can tell when the operation is complete by removing the beaker, blowing the gas away from the surface of the liquid, and observing if a strong odor of hydrogen sulphide is given off. If the odor is very strong, it indicates that the precipitation is complete.

Allow the precipitate to settle, and then, without disturbing the precipitate, lead a little more of the hydrogen sulphide through the clear liquid, to be sure that the metals of this group are completely precipitated. If a precipitate is formed, the treatment with hydrogen sulphide must be continued until precipitation is complete. Allow the precipitate to settle and pour as much as possible of the clear liquid through the filter without disturbing the precipitate. When the liquid has run through, wash the precipitate on to the filter with hot water and wash twice on the filter with hot water. Set the filtrate aside, to be treated for Group III. The precipitate may contain metals of either Division A or Division B, or may contain both. As the methods of separating the metals of the two divisions differ, we should always ascertain whether both divisions are present or not, and if metals belonging to but one division are present, we should learn to which division they belong before treating the whole precipitate. To do this, remove a portion of the damp precipitate about as large as a small pea to a small porcelain

dish, and add about one cubic centimeter of ammonia, and from half a dozen drops to half a cubic centimeter of yellow ammonium sulphide, depending upon the color of the precipitate. If the precipitate is light colored, only a few drops of the yellow sulphide is needed, or a little more of the common ammonium sulphide may be substituted; but if it is rather dark, indicating that tin may be present, more of the yellow sulphide must be used. In either case heat gently and stir with a glass rod for a few minutes. If all the precipitate dissolves, Division B alone is present. If it does not all dissolve, the insoluble part belongs to Division A.

This is filtered, washed once with hot water, and the filtrate rendered slightly acid with hydrochloric acid. Sulphur will be thrown out by the hydrochloric acid. If it merely makes the solution milky, it may be disregarded, but if the solution is colored yellow, it shows the presence of some of the members of Division B, and in this case the two divisions must be separated. If only metals belonging to one of the divisions are present, the precipitate is at once treated as described for the separation of the metals of that division.

97. Separation of the Two Divisions of Group II.— The precipitate is removed, as completely as possible, from the filter to a porcelain dish. If the precipitate is dark colored, it may contain tin, and in that case from 2 to 3 cubic centimeters of yellow ammonium sulphide are added, then about an equal amount of common ammonium sulphide, and finally a little more than enough ammonium hydrate to cover the precipitate is added. In case the precipitate is light colored, stannous sulphide must be absent, and in that case only a few drops of the yellow sulphide should be added, and the quantity of common ammonium sulphide should be increased about the same amount that the yellow sulphide is decreased. In either case, gradually heat the mixture, while it is being stirred, until it begins to boil. By this time the metals of Division B will all be in solution. Add to this about twice its volume of hot water, and after allowing it to stand for a few moments to settle, filter it, and wash several

times with hot water. The precipitate will now contain the members of Division A, and the filtrate contains the metals of Division B.

98. Separation of the Metals of Division A.—This precipitate—or the original precipitate, if it were found to contain only the metals of Division A—is removed as completely as possible to a small porcelain dish, and covered with a mixture of equal parts of concentrate and dilute nitric acid. It should be heated slowly and with constant stirring until it boils. The sulphides of lead, copper, cadmium, and bismuth will be dissolved, while the sulphide of mercury remains as a black, insoluble precipitate. Sulphur will also be thrown out during the solution of the sulphides, but this may easily be recognized, and is disregarded. It generally collects in a pasty mass, which may be somewhat colored by small quantities of undissolved sulphides. The excess of acid is evaporated off, and about 25 cubic centimeters of hot water is added. Filter, and wash two or three times with hot water. A black precipitate indicates mercury, but it should be confirmed by dissolving a little of the precipitate in aqua regia, evaporating the excess of acid, diluting slightly, and testing with stannous chloride. Other tests for mercury may also be applied. The filtrate, containing the metals whose sulphides are soluble in nitric acid, is treated with a few drops of sulphuric acid, to test for lead. If a precipitate is formed, continue the addition of the sulphuric acid, drop by drop, till all the lead is precipitated as sulphate. Filter, wash once, and confirm the presence of lead by the solubility of the sulphate in tartaric acid and ammonia, as directed in Art. **20**, 8.

A slight excess of ammonia is now added to the filtrate. Bismuth, if present, will be precipitated as white bismuth hydrate, while copper and cadmium, if present, form precipitates that are at once dissolved in excess. If the solution assumes a deep-blue color, it is conclusive evidence of the presence of copper. The precipitate, if one is formed, is probably bismuth, but if the lead was not all removed, it will be precipitated at this point, and if the third-group metals

were not thoroughly washed out of the original precipitate, they may come down here, so we must confirm the presence of bismuth. To do this, dissolve a little of the precipitate in a few drops of hot concentrate hydrochloric acid in a test tube, and drive off most of the acid by heating. Pour a few drops of this solution, a drop at a time, into a test tube nearly filled with cold water. If a white precipitate is formed, it is conclusive evidence of the presence of bismuth; but if too much acid were left in the bismuth solution, no precipitate will be formed. In that case a little hydrogen sulphide is added to the acid solution in the test tube of water that failed to give a precipitate. A brown precipitate confirms bismuth, while the absence of a brown precipitate proves that it is not present.

The ammoniacal filtrate is next examined for copper and cadmium. If it is colored blue, copper is present, but if colorless, it shows the absence of copper. In that case, to a small quantity of it in a test tube, add hydrogen sulphide, which will precipitate cadmium, if present, as yellow cadmium sulphide. If the solution is blue, a little of it is taken in a test tube, and just enough potassium-cyanide solution added to entirely destroy the color. To this colorless solution add hydrogen sulphide, which will precipitate cadmium, as yellow cadmium sulphide, but will not precipitate copper from the cyanide solution.

In separating the cadmium and copper by this method, traces of other metals are sometimes present, and give the cadmium sulphide a dark color. For this reason some chemists prefer the following method of separating them.

Render the filtrate from the bismuth slightly acid with hydrochloric acid, and pass a current of hydrogen-sulphide gas through it till the copper and cadmium are both completely precipitated. Filter and wash the precipitate two or three times with hot water and a few drops of hydrogen-sulphide solution. Remove the precipitate to a porcelain dish as quickly as possible, in order to avoid the oxidizing action of the air, treat it with warm dilute sulphuric acid, and bring to boiling in order to expel the hydrogen sulphide

generated by the action of the sulphuric acid upon the sulphides. Cadmium sulphide will be dissolved, while copper sulphide remains as a black insoluble compound. It should be filtered at once, and the precipitate examined for copper, by dissolving it in nitric acid and applying the reactions given for copper. To test the filtrate for cadmium, add ammonia in sufficient quantity to render the solution alkaline, and then add just enough hydrochloric acid to render it distinctly acid, and again pass a current of hydrogen sulphide through it, when cadmium, if present, will be precipitated as yellow cadmium sulphide. This method is more difficult to perform properly than the first method given.

99. Separation of the Metals of Division B.—1. The metals of Division B are in solution in the filtrate from the metals of Division A. This filtrate is rendered acid with hydrochloric acid, when more or less sulphur is thrown out, depending on the amount of yellow ammonium sulphide used, and the metals are precipitated as yellow or orange-colored sulphides. The hydrochloric acid must be added as long as a precipitate is formed. When precipitation is complete, filter and wash the precipitate two or three times with hot water. When the water has run through, remove the precipitate to a porcelain dish, and add enough concentrate hydrochloric acid to cover the precipitate. Heat until it has boiled for two or three minutes, when the sulphides of tin and antimony will be dissolved and all the hydrogen sulphide expelled. The arsenic will remain as a yellow sulphide and some free sulphur will be thrown out.

In case the original precipitate contained only metals of Division B, it should not be treated with sulphides, but should be transferred to a porcelain dish at once, and treated with hydrochloric acid, as just described.

The hydrochloric-acid solution is diluted with about twice its volume of water, filtered, and the precipitate washed twice on the filter with hot water. The arsenic, if present, will be in the precipitate, and antimony and tin in the filtrate. Remove the precipitate to a small porcelain dish

and add a small amount of concentrate nitric acid. If the precipitate is so small that it cannot be removed from the filter, the part of the paper containing the precipitate may be placed in the dish and the acid added. In either case, heat until the precipitate is dissolved and most of the acid is driven off; then add a little water and filter to remove free sulphur and filter paper, receiving the filtrate in a test tube. Then place a little magnesium sulphate in another test tube, precipitate it with ammonia, using considerable excess, and dissolve the precipitate thus formed by adding ammonium chloride. To this solution add some of the filtrate from the other tube, taking care that the solution remains alkaline, and shake violently. A white, crystalline precipitate proves the presence of arsenic.

Another method often used to confirm arsenic, is to remove a little of the precipitate, supposed to be As_2S_3, to the charcoal and heat it before the blowpipe. Dense white fumes, with a garlic odor, prove the presence of arsenic.

To examine the acid filtrate for tin and antimony, place in it several pieces of zinc, and when the acid begins to act on them, place a piece of platinum foil in contact with one of the pieces of zinc and leave it thus for a few seconds. If antimony is present, some of it will be deposited on the platinum, forming a black stain. Remove the platinum and allow the acid to act on the zinc, until all chemical action ceases, and some zinc remains undissolved. During this action some of the antimony escapes as SbH_3, and the rest is deposited on the zinc as metallic antimony, in the form of a black powder. The tin is all deposited either as a gray powder or as a gray, spongy mass of metallic tin. The pieces of zinc are now removed and the adhering metals are washed back into the dish and allowed to settle. Decant the clear liquid, and wash two or three times by decantation, finally decanting as much of the water as possible. Add a little concentrate hydrochloric acid and heat to boiling. The tin will dissolve to stannous chloride, while the antimony remains unchanged. Add a little water and filter, receiving the filtrate in a test tube. This is tested for stannous chloride by means of

mercuric chloride, and by other reactions for stannous compounds.

The antimony is further confirmed by dissolving a little of the black powder in aqua regia, driving off the excess of acid, diluting with water, and precipitating with hydrogen sulphide. If a white precipitate is formed when water is added to dilute the solution, this in itself is proof of antimony.

2. The metals of this division are sometimes separated by another method. In this case the precipitated sulphides of Division B, after washing on the filter, are transferred to a porcelain dish, a saturated solution of acid ammonium carbonate is added in sufficient quantity to cover the precipitate, and this is heated for a few minutes, with constant stirring. The arsenic is changed into the two soluble compounds, ammonium sulphoarsenite and ammonium arsenite, while the antimony and tin remain unchanged. Filter, and wash two or three times with hot water. The precipitate will contain the antimony and tin, and the arsenic will be in the filtrate. The precipitate is removed to a porcelain dish, dissolved in concentrate hydrochloric acid, and the tin and antimony separated as described in the first method.

The alkaline filtrate is treated with an excess of hydrochloric acid, when arsenic, if present, will be precipitated as yellow arsenious sulphide. This is sufficient evidence of arsenic, but it may be confirmed by either of the methods previously given.

GROUP III.

100. The filtrate from Group II, or, in case the *side test* showed that the solution did not contain any of the metals of Group II, the filtrate from Group I is next treated for Group III. If the second group has been precipitated from this solution, it will contain hydrogen sulphide, which must be expelled by boiling, before adding ammonia, or ammonium sulphide will be formed, and the fourth group be precipitated with the third. If the solution is growing too large, it is best to boil it in a beaker, thus concentrating the solution at the same time that the hydrogen sulphide is driven off. But if

the solution is not too large, it is best to boil it in a flask. The student must be sure that all the hydrogen sulphide is expelled before proceeding. The odor of the vapor is a good indication, or a piece of filter paper saturated with a solution of lead or silver, held in the vapor driven off by the heat, will be colored as long as hydrogen sulphide is present. If sulphur is thrown out in the solution during this operation, it should be filtered off before proceeding.

There are several things that may complicate the separation of the metals of this group. Manganese may be partially precipitated with this group, and if phosphoric or oxalic acid is present, the phosphates or oxalates of the alkaline earths are either partly or wholly precipitated when ammonia is added. In the presence of phosphoric acid, part of the iron and aluminum are precipitated as phosphates, and barium, strontium, calcium, and magnesium phosphates may also be precipitated. When oxalic acid is present, the oxalates of barium, strontium, and calcium are precipitated with this group. Fortunately, these acids do not ordinarily occur in solutions that are treated for the group separations, and the student may never have to separate the metals in a solution containing them, but in case he should meet them in a solution, methods for the treatment of this group, when they are present, are given, after describing the ordinary method for the separation of the metals of this group.

In any case the solution is heated to boiling and a few drops of concentrate nitric acid are added, to oxidize ferrous compounds to ferric. If a brown color is formed, continue to add the acid, drop by drop, and boil till the solution becomes clear. Now add about 10 cubic centimeters of ammonium chloride, and then slowly add ammonium hydrate in slight but distinct excess, while the solution is constantly stirred. Continue the boiling for about one minute, and be sure that the solution still smells distinctly of ammonia. Filter as soon as the precipitate has partly settled, while the solution is still hot, and wash two or three times with hot water. The filtrate is now ready to be treated for Group IV, and the precipitate should be tested for phosphoric and

oxalic acids. If they are found to be present, the precipitate is treated as described later. If they are absent, the metals are separated by the usual method.

101. Ordinary Method of Separating the Metals of Group III.—If iron is present in the solution, some of the manganese will generally be precipitated with the iron. To test for manganese, remove a small portion of the precipitate to the platinum foil, and fuse with sodium carbonate and potassium nitrate, as directed in Art. **67.** A dark-green color proves the presence of manganese, which is sufficient if we merely want to know whether it is present in the solution or not. But if we wish to separate it from the metals of this group, the whole precipitate is removed to a beaker and dissolved in about 25 cubic centimeters of hydrochloric acid by the aid of heat. Bring this solution to boiling, precipitate with a slight excess of ammonia, and filter at once. Wash the precipitate on the filter once with hot water, and add this filtrate to the one previously obtained, to be treated for Group IV. The precipitate will contain the metals of Group III.

A small portion of the precipitate is dissolved in hydrochloric acid, the solution diluted a little, and potassium ferrocyanide added, when iron, if present, will give a characteristic blue precipitate, which is conclusive proof of the presence of iron.

The remainder of the precipitate is now removed to a beaker and dissolved in dilute hydrochloric acid, by the aid of heat, using as little acid as possible. When all is dissolved, add considerable excess of sodium hydrate, and bring to boiling. This will dissolve the aluminum hydrate at first formed, while the iron and chromium remain as a precipitate. Filter and wash two or three times with hot water on the filter. Test the precipitate for chromium by fusing a little of it on the platinum foil, as directed in Art. **56.** The bead test may also be used for both chromium and manganese. There are two good methods of testing the filtrate, and, as a rule, both should be used. They are:

1. Place a little of the alkaline filtrate in a test tube, add ammonium chloride, shake well, and stand aside for a minute or two. If aluminum is present, it will be precipitated as white aluminum hydrate, but it may take a few moments to collect so that it is readily seen.

2. Render the remainder of the filtrate slightly acid by means of concentrate hydrochloric acid, add a slight excess of ammonium carbonate, boil the solution a moment to expel the liberated carbon dioxide, and allow to settle. If aluminum is present, it will be precipitated as white aluminum hydrate. When the precipitate is first formed, it is almost colorless, and may be overlooked unless the mixture is examined carefully. After standing a while, it is much more easily seen, especially when the tube, or beaker, is moved sufficiently to cause the precipitate to move through the liquid in which it is suspended.

102. Treatment of Group III, When Phosphoric Acid is Present.—To test for phosphoric acid, remove a little of the original precipitate on the point of a knife blade to a porcelain dish, and dissolve it in a drop or two of nitric acid. Place about two or three cubic centimeters of ammonium-molybdate solution in a test tube, heat it to the boiling point, and add a drop or two of the solution obtained by treating the precipitate with nitric acid. A yellow precipitate proves the presence of phosphoric acid, while the absence of a yellow precipitate proves its absence.

When phosphoric acid is present, the precipitate is removed to a porcelain dish and dissolved in the least necessary quantity of hydrochloric acid, by the aid of heat, an excess of sodium hydrate is added, and the whole is heated to boiling. This dissolves the aluminum hydrate and phosphate, and the other metals remain in the precipitate. Filter, wash once with hot water on the filter, and test the filtrate for aluminum by the methods previously described.

Remove the precipitate to a porcelain dish, dissolve it in concentrate nitric acid, and add an excess of pure tin foil. Heat to boiling, and stir well. The phosphorus and tin

form an insoluble compound, while all the metals are changed to soluble nitrates. Filter, wash with hot water, and then throw away the precipitate, which contains only the tin and phosphorus. Add about 10 cubic centimeters of ammonium chloride to the filtrate, heat it to boiling, and precipitate with a slight excess of ammonia. Filter, wash once with hot water, and add the filtrate to the first filtrate, to be treated for Group IV. Examine the precipitate for iron and chromium, as previously directed.

103. Treatment of Group III, When Oxalic Acid is Present.—To examine the precipitate for the presence of oxalic acid, dissolve a small portion of it in a test tube, in a few drops of concentrate nitric acid, add an excess of sodium carbonate, and boil for a few moments. The metals are precipitated as carbonates and hydrates, and the oxalic acid unites with the sodium, forming soluble sodium oxalate. Filter, acidify the filtrate with acetic acid, boil till all the carbon dioxide is driven off, and add calcium chloride. If oxalic acid is present, the calcium will be precipitated as white calcium oxalate, which is insoluble in acetic acid, but is readily dissolved by hydrochloric acid. In making this test, care must be taken to render the filtrate distinctly acid with acetic acid, and to boil till all carbon dioxide is expelled, otherwise calcium carbonate will be precipitated, and this will be mistaken for calcium oxalate.

If oxalic acid is found to be present, the precipitate is dissolved, and the aluminum removed, just as described in the case where phosphoric acid is present. The precipitate from the sodium hydrate is removed to a porcelain dish, an excess of sodium carbonate added, and boiled for a minute or two. The metals are thus changed to insoluble hydrates and carbonates, and the oxalic acid unites with the sodium, forming soluble sodium oxalate. Filter, and wash two or three times with hot water. The filtrate may be thrown away.

Transfer the precipitate to a beaker, dissolve it in dilute hydrochloric acid, bring to boiling, and precipitate the iron and chromium with a slight excess of ammonia. Filter,

wash once on the filter with hot water, and add the filtrate to the first filtrate from the separation of this group, which is to be treated for the fourth group. The precipitate is examined for iron and chromium by the methods already described.

GROUP IV.

104. The filtrate from Group III, or, in case there were none of the metals of Group III in the solution, the filtrate from Group II, which failed to give a precipitate with ammonia, is next treated for Group IV. But before adding the group reagent to the whole quantity, a small amount is taken out in a test tube and ammonium sulphide added, as this will save boiling off the ammonium sulphide, and filtering from sulphur, in case none of the metals of Group IV are contained in the solution. If this side test yields no precipitate, it is thrown out and the main filtrate is treated for Group V. If we find, by the side test, that metals of the fourth group are present, the filtrate from Group III is heated to boiling and precipitated by ammonium sulphide. It is important to avoid a large excess of this reagent, but a sufficient quantity must be added to precipitate all the metals of this group. It is difficult to tell when just enough of the reagent has been added, but a sufficient quantity is indicated if the solution retains a distinct odor of the reagent after stirring a few moments. As a safeguard, the filtrate must always be tested by adding to it a few drops of the reagent, and if a precipitate is formed, the addition of the reagent is continued till the precipitation is complete, and this precipitate is added to and treated with the first one.

When the precipitation is complete, boil the contents of the beaker for a moment, remove the beaker from the gauze, allow the precipitate to completely settle, decant the clear liquid as completely as possible through the filter, wash the precipitate on to the filter with hot water, and wash twice on the filter with hot water. Care must be taken to expose the precipitate to the air as little as possible, as the air tends to oxidize the sulphides to soluble sulphates. To avoid this, a

drop or two of ammonium sulphide is sometimes added with the water on the filter, but if the whole operation is performed quickly, and with little exposure to the air, this is generally unnecessary.

The filtrate is set aside to be treated for Group V, and the precipitate is examined for the metals of Group IV. By observing the color of the precipitate, we may sometimes avoid useless work. If the precipitate is light colored, only zinc and manganese can be present, and in that case we dissolve the precipitate and proceed at once to separate the zinc and manganese, as directed later. In case the precipitate is black, all the metals of the group may be present, and we must examine the precipitate for all of them. To do this, punch a hole in the apex of the filter with a stirring rod, and wash the precipitate through into a beaker or porcelain dish, using about 30 cubic centimeters of cold water. To this add about 5 cubic centimeters of dilute hydrochloric acid, and stir for a minute or two in the cold. The sulphides of zinc and manganese are dissolved, while the sulphides of cobalt and nickel are not attacked by this dilute acid. Filter, and wash twice on the filter. The precipitate will contain the cobalt and nickel, and the filtrate, the zinc and manganese, if all were present. To learn if cobalt is present in the precipitate, the borax-bead test is used, as described in Art. **59.** Nickel also gives some color to the bead; so that, if a distinct blue is not obtained, the result should be rejected and a further examination made. If the bead proves the absence of cobalt, a little of the precipitate is dissolved in a few drops of aqua regia, nearly all the acid driven off, a little water added, and the solution thus made is tested for nickel by adding sodium hydrate. A green precipitate proves the presence of nickel. The other reactions for nickel may also be used to further confirm it.

When cobalt is present, it must be removed before we can test for the nickel. To do this, remove the precipitate to a small porcelain dish—on a small portion of the filter if necessary—and dissolve it in a few drops of aqua regia. Evaporate nearly all the acid, add about 1 cubic centimeter of water,

and filter into a test tube, using a little more water to wash the filter paper, which should be very small. Neutralize this solution with concentrate ammonia, then render it slightly, but distinctly, acid with acetic acid, add a stick of potassium nitrate that will reach nearly to the top of the solution, and allow it to stand for several hours. The cobalt will all be precipitated as a yellow powder, which will settle to the bottom of the tube, and the clear liquid may be examined for nickel by means of sodium hydrate, and by other tests.

The acid filtrate is next examined for zinc and manganese. It is first boiled, to expel all hydrogen sulphide, then rendered strongly alkaline with sodium hydrate, and heated to boiling. Both zinc and manganese are at first precipitated as light-colored hydrates. The manganese is quite rapidly oxidized to a brown compound, while the zinc is dissolved in the excess of sodium hydrate. Filter and test the precipitate for manganese, and the filtrate for zinc. The precipitate may be tested by means of the borax bead, and also by fusing part of it on the foil with sodium carbonate and potassium nitrate. The filtrate may be tested by hydrogen sulphide. If this gives a white precipitate, it is sufficient evidence of zinc.

GROUP V.

105. The filtrate from the fourth group is boiled till the ammonium sulphide is completely decomposed, and filtered from sulphur, if any is deposited during the boiling. In case there were no fourth-group metals in the solution, this boiling will be unnecessary, as there will be no ammonium sulphide in the solution. We can tell when all the sulphide is driven off in this case by the same methods that were used for the purpose when the filtrate from the second group was boiled to expel the hydrogen sulphide.

The clear filtrate is rendered distinctly alkaline with ammonia, heated, and ammonium carbonate is added in sufficient quantity to completely precipitate the barium, strontium, and calcium, as carbonates. The contents of the beaker are boiled for a few moments in order to change any acid carbonates

that may be formed at first, into normal carbonates, but this boiling must not be continued more than a minute at the outside, or the ammonium chloride in the solution will begin to dissolve the carbonates by changing them to chlorides. The precipitate is allowed to settle before filtering. It is washed twice on the filter with hot water, and then examined for the members of this group. The filtrate is set aside to be treated for Group VI.

Remove the precipitate to a beaker and dissolve in a slight excess of acetic acid, by the aid of gentle heat. Remove a little of this solution to a test tube, and add potassium chromate to test for barium. If a yellow precipitate is formed, it shows the presence of barium. In this case, add potassium chromate to the rest of the acetic-acid solution in sufficient quantity to precipitate all the barium. Filter and wash once or twice on the filter. A yellow precipitate at this point is proof of barium, but it may be confirmed by holding a little of it on the loop of a platinum wire in a non-luminous Bunsen flame and noting the color imparted to the flame. It is well, after holding it in the flame for a while, to dip the loop containing the dry precipitate into some dilute hydrochloric acid, and then return it to the flame. The acid will partly dissolve the chromate, forming barium chloride, which is quite volatile, and, therefore, colors the flame much more distinctly. If desired, the rest of the chromate precipitate may now be dissolved in dilute hydrochloric acid, and other tests for barium applied.

The filtrate, which may contain strontium and calcium, is precipitated by ammonia and ammonium carbonate, in exactly the same way that the original group precipitation was made. Filter, and wash the precipitate well to free it from the soluble chromates. Dissolve the precipitate in a little hydrochloric acid, and make a preliminary flame test, by holding a drop of the solution in the flame, on the loop of the platinum wire. If strontium is present, there will be a flash of bright-red light, while calcium imparts a brick-red color to the flame. If the calcium solution is very strong, its flame may be mistaken for the strontium flame.

To separate the strontium and calcium, dilute the solution to from 50 to 75 cubic centimeters, and add ammonium sulphate. Strontium, if present, will be slowly precipitated as white strontium sulphate, while the calcium remains in solution. After letting it stand for some time, for the precipitate to form and settle, filter and test the precipitate for strontium by means of the flame. If the color is not imparted to the flame at once, the precipitate is held in the reducing flame for a time, until the sulphate is partly reduced to sulphide. Then, if it is dipped in dilute hydrochloric acid and quickly withdrawn, the sulphide is partly changed to chloride, which is quite volatile and colors the flame quickly and distinctly.

The filtrate is now rendered distinctly ammoniacal, heated to boiling, and ammonium oxalate added. If calcium is present, a white, crystalline precipitate of calcium oxalate, which is insoluble in acetic acid, is formed. This precipitate proves the presence of calcium, while a failure to obtain this precipitate proves its absence. If the precipitate is obtained, however, it may be further verified by the color it imparts to the flame, as in the case of barium and strontium.

106. Second Method of Separating Strontium and Calcium.—Another method of separating strontium and calcium, based upon the solubility of calcium sulphate in ammonium sulphate, is sometimes used. In this method the barium is removed by potassium chromate, the strontium and calcium precipitated by ammonium carbonate, and washed on the filter to free the precipitate from potassium chromate, as described above. Dissolve this precipitate in the least necessary quantity of hydrochloric acid, and add a little water, but leave the solution quite concentrate. To this solution add dilute sulphuric acid in sufficient quantity to precipitate all the strontium and calcium as sulphates, and allow it to stand for the precipitate to form and settle. Filter, and wash once on the paper. If only a trace of calcium is present, the filtrate should be tested. Otherwise, it may be disregarded.

Remove the precipitate to a porcelain dish, cover it with a concentrate solution of ammonium sulphate,* and heat gently for about 10 minutes, with frequent stirring. This will dissolve the calcium sulphate, while the strontium sulphate is not acted upon. Filter, and wash two or three times, preferably with warm water. Test the precipitate for strontium in the usual manner, and examine the filtrate for calcium by means of ammonium oxalate, as described above.

GROUP VI.

107. If, at the time of the precipitation of the fifth group, the boiling was not continued long enough, or exceeded the proper time, the filtrate may contain traces of barium, strontium, and calcium; so, before treating this filtrate for the sixth group, 2 or 3 drops of sulphuric acid and a like amount of ammonium oxalate are added, and the solution boiled for a few moments, taking care that it remains distinctly alkaline. If a slight precipitate forms, it is filtered off. The filtrate can now only contain the sixth and seventh groups. It should be concentrated to 75 or 100 cubic centimeters before precipitating. Add a few cubic centimeters of concentrate ammonia, and then sodium phosphate; stir well, and let stand for some time for the precipitate to form and settle. If the solution is very dilute, this may require several hours, and, at all events, the solution should stand until it becomes perfectly cold. The presence or absence of a precipitate at this point is proof of the presence or absence of magnesium, but if a precipitate is formed, magnesium may be confirmed by treating a little of it on the charcoal before the blowpipe, as directed in Art. **79.**

GROUP VII.

108. As the alkalies have been added to the solution in the form of reagents, we cannot use the filtrate from the sixth group to test for the members of the seventh, but must

* Ammonium-sulphate solution for this purpose is made by dissolving about 15 grams of the solid in 30 cubic centimeters of water.

take small portions of the original solution. We should first test for ammonium. To do this, take a small quantity of the original solution in a test tube, add about an equal amount of sodium hydrate, and boil. Ammonium compounds, when present, are always decomposed, yielding ammonia gas NH_3, which is recognized by its odor, by the white fumes that are formed when in contact with hydrochloric acid, and by its power of turning red litmus paper blue. The odor is by far the best proof, for nothing else has a similar odor.

A second small quantity of the original solution is now taken, a clean platinum wire that has just been tested in the flame to prove the absence of alkalies, is dipped into it and the drop of solution adhering to the loop is brought into the non-luminous flame.

Sodium is recognized by the intense yellow color that it imparts to the flame, while potassium is recognized by the violet color that is given to the flame by its compounds.

If both sodium and potassium are present in a solution, the violet potassium flame is entirely obscured by the intense yellow flame produced by the sodium. But if the flame is viewed through a thick, blue (cobalt) glass, the yellow rays of the sodium are entirely absorbed and the potassium flame is distinctly seen. A still better method of recognizing sodium and potassium, is by means of the spectroscope, which will be described later.

GENERAL DIRECTIONS.

109. We now have before us a method by which any number of the common metals may be recognized in, and separated from, solutions containing a mixture of metals, ***but the student should not expect to become an expert analyst from merely reading directions. He should make up mixtures and separate them according to the scheme given, following directions as closely as possible.***

The operations are described as carefully as possible, but a student must perform each of them, with known solutions,

carefully observing the behavior of each metal or group of metals, before he can be absolutely certain that his results are correct when working on an unknown solution.

The student will also find that he can learn the method much more easily and thoroughly by carrying out each operation as he studies it, using the description given as a guide in his work.

Mixed solutions for practice can easily be prepared by mixing some of the solutions made as described for the reactions of the separate metals. In doing this, certain simple precautions must be taken; as, for example, chlorides must not be introduced into solutions containing first-group metals, or these metals will at once be precipitated as chlorides. Sulphates must not be added to solutions containing lead, mercurous, barium, strontium, or calcium compounds, or these metals will be precipitated as sulphates. Arsenites and arsenates, under certain conditions, precipitate some of the metals, so care should be exercised in making solutions containing these. Much valuable experience will be acquired in making up these solutions, if the work is done thoughtfully.

The student should not make up too complicated a solution at first. In fact, it is best to start with a solution containing only metals of the first group, and after these have been separated, make up more complicated mixtures, but avoiding the more difficult operations until considerable familiarity with the work has been acquired.

Each student is strongly advised to make up and analyze the following list of solutions in their order, using, in making these mixtures, the solutions already made up for the reactions of the separate metals. They should be used as soon as possible after being made up, as some of them decompose upon standing.

1. *Lead*, *silver*, and *mercurous*.

This is made by mixing equal parts of the nitrates of the three metals.

2. *Lead*, *bismuth*, and *cadmium*.

This is made by mixing solutions of the nitrates of the three metals in equal proportions.

3. *Antimony*, *arsenic*, and *tin*.

To prepare this, mix antimony chloride, stannous chloride, and sodium arsenite, in equal amounts. If a precipitate is formed, dissolve it in the least necessary quantity of concentrate hydrochloric acid.

4. *Iron*, *aluminum*, and *chromium*.

This is made by mixing equal quantities of the solutions of ferrous sulphate, common alum, and chrome alum. The alums will introduce a little potassium or ammonium, or perhaps both, and the student should examine the solution for these as well as for the constituents that were intentionally introduced.

5. *Aluminum*, *nickel*, and *zinc*.

To prepare this, mix equal amounts of the solutions of alum, nickel nitrate, and zinc sulphate. This solution, like the preceding one, should be examined for potassium and ammonium.

6. *Barium*, *strontium*, and *calcium*.

This is generally made by mixing barium chloride, strontium nitrate, and calcium chloride, in equal quantities. But either the chlorides or nitrates may be used equally well.

7. *Magnesium*, *ammonium*, *potassium*, and *sodium*.

This solution is generally a mixture of equal parts of the solutions of magnesium sulphate, and ammonium, potassium, and sodium nitrates, but almost any compounds of these metals will answer the purpose.

This list is given as a guide to the student in starting in the group separations, and, after completing it, he should make up and analyze a number of solutions, until he has determined all of the metals, a few at a time, or he can get a friend to make up solutions for him, and thus analyze them before knowing their composition.

The student must never forget to look for the alkalies, whether he finds other metals in the solution or not. A portion of the original solution should first be tested for ammonium with sodium hydrate, and then another portion tested for sodium and potassium in the flame.

The student should never attempt to separate the two

divisions of the second group until he is thoroughly familiar with the separation of the metals of each division, as this is one of the most difficult operations in qualitative analysis.

The sulphides of some of the metals occasionally become slimy at this point and pass through the filter. Boiling, and allowing to settle again, sometimes remedies this, but, as a rule, this portion of the solution must be thrown away, and the analysis begun again with a fresh portion of the original solution. However, after the student gains a little experience in chemical manipulation, this trouble will be very rare.

The separation of Group III, and subsequent groups, in the presence of phosphoric or oxalic acid, should never be attempted until the operator is thoroughly familiar with all the separations when they are absent.

While the main object in this, as in every part of the work, is to become able to analyze substances, it is not the only object. And, although definite directions are given for the separation of the groups, the directions should not be followed blindly and without thought. This system of separating the metals is built upon the properties of their compounds, and their deportment with reagents, as previously described; and the many chemical relations, here brought together in a small space, should be carefully studied. It is only by such study that the student will acquire that knowledge of chemical relations which is essential in all advanced chemical work.

ACIDS.

COMMON INORGANIC ACIDS.

110. Having learned to recognize and separate the metals, the next step is to learn to recognize the acids in a similar manner. As most of the substances that a chemist is called upon to analyze are compounds, he must be able to determine the acid as well as the metal, and, in order to have the conditions as nearly the same in practice as in actual

work, the acids should be determined in compounds rather than to work on free acids.

The reactions for the common inorganic acids will be given first, then the reactions for the common organic acids. These will be followed by the reactions for the less common inorganic and organic acids.

The student should verify and become familiar with the reactions for the common acids, both inorganic and organic. This can only be accomplished by actually performing the operations, as in the case of the metals.

The reactions for the less common acids are given more as a matter of reference, so that if the student is called upon to determine them at any time, he will have directions for doing so.

HYDROCHLORIC ACID.

111. Hydrochloric acid HCl, and all chlorides, except lead, silver, and mercurous chlorides, are soluble in water. Ammonium chloride or sodium chloride may be used for the reactions.

1. *Silver nitrate* precipitates white silver chloride from solutions of hydrochloric acid or chlorides. This precipitate gradually turns to brown upon standing for some time in the light, or is changed much more rapidly by heating. It is soluble in ammonia or potassium cyanide, and is reprecipitated from these solutions by nitric acid.

2. *Lead acetate* precipitates white lead chloride $PbCl_2$ from solutions that are not too dilute. Lead chloride is somewhat soluble in cold water, so it is not completely precipitated. It is soluble in hot water, and, upon cooling, crystallizes from this solution in white needles.

3. *Mercurous nitrate* precipitates white mercurous chloride Hg_2Cl_2, which is not dissolved by dilute acids, but is soluble in hot concentrate nitric acid. Ammonia changes this precipitate to black amido-mercurous chloride Hg_2NH_2Cl.

4. Solid chlorides, when heated in a test tube with concentrate sulphuric acid, are decomposed, yielding free hydrochloric acid, which may be recognized by its odor. If

a glass rod be dipped in ammonia, and then brought to the mouth of the tube, dense white fumes of ammonium chloride are formed.

HYDROBROMIC ACID.

112. Hydrobromic acid HBr forms compounds similar to those of hydrochloric acid, but they are not so common. All the common bromides, except those of silver, lead, and mercury, are soluble in water. Potassium bromide or sodium bromide may be used for the reactions.

1. *Silver nitrate* precipitates yellowish-white or light-yellow silver bromide $AgBr$ from solutions of bromides or hydrobromic acid. This precipitate is insoluble in dilute acids, dissolves with some difficulty in ammonia, but is easily soluble in potassium cyanide.

2. *Lead acetate* precipitates white lead bromide $PbBr_2$, which is less soluble in water than the corresponding lead chloride, but is dissolved by nitric acid.

3. *Mercurous nitrate* precipitates yellowish-white mercurous bromide Hg_2Br_2.

4. Most bromides in the solid state, or in concentrate solutions, when heated with concentrate sulphuric acid, are decomposed and give off a brownish-red vapor of free bromine.

5. All bromides, with the exception of silver bromide, are decomposed when heated in a test tube with concentrate nitric acid, yielding free bromine. If a solution of a bromide is treated, it is colored yellow, yellowish red, or brownish red, according to the degree of concentration. If a solid bromide, or a very concentrate solution is treated with the nitric acid, brownish-red vapors are given off, which collect in the upper part of the tube in heavy, reddish globules of free bromine. This is the most characteristic reaction for hydrobromic acid.

HYDRIODIC ACID.

113. The iodides correspond in many respects with the chlorides and bromides, but many more of the iodides of the heavy metals are insoluble in water than is the case with the

chlorides and bromides. The iodides of silver, lead, mercury, bismuth, antimony, tin, and arsenic, are either insoluble, or soluble with difficulty, in water. The others are more or less easily dissolved. Potassium iodide is best used for the reactions.

1. *Silver nitrate* precipitates yellowish-white silver iodide AgI, which becomes dark upon standing in the light. It is insoluble in dilute nitric acid, and only slightly soluble in ammonia, but is dissolved by potassium cyanide.

2. *Lead acetate* precipitates yellow lead iodide PbI_2, which, like lead chloride, is soluble in hot water.

3. *Mercurous nitrate* precipitates greenish-yellow mercurous iodide Hg_2I_2, which is soluble in excess of potassium iodide; hence, no permanent precipitate is formed until an excess of mercurous nitrate has been added.

4. *Mercuric chloride*, when added in the proper amount, produces a scarlet precipitate of mercuric iodide HgI_2, which is soluble in an excess of either the potassium iodide or mercuric chloride, but is insoluble in nitric acid.

5. *Copper sulphate* mixed with *sulphurous acid* gives a dirty-white precipitate of cuprous iodide Cu_2I_2. Chlorides and bromides are not precipitated by this reagent; hence, it is a convenient method of testing for iodides in their presence. Instead of copper sulphate and sulphurous acid, we may use a solution, made by mixing 1 part of copper sulphate with $2\frac{1}{2}$ parts of ferrous sulphate, and dissolving them in water, as this solution produces the same precipitate.

6. To test for iodine in a very dilute solution, acidify the solution with sulphuric acid, add a few drops of starch solution or starch paste,* and then a few drops of a strong solution of potassium nitrate. If iodine is present, the solution will assume a deep-blue color, owing to the formation of blue starch iodide.

7. All iodides in the solid form, when heated with concentrate sulphuric acid in a test tube, are decomposed,

* Starch paste may be made by grinding up a little pure starch with water, or a solution may be made as described in Art. **80**, Experiment 43, *Inorganic Chemistry*, Part 1.

yielding a characteristic violet vapor of iodine, which collects in a solid mass on the sides of the upper part of the tube. Near the edges, where the layer is very thin, this appears violet, but where the layer is thicker it looks black.

SULPHURIC ACID.

114. Sulphuric acid H_2SO_4 is a very strong acid. It forms stable compounds with the metals, and is not replaced in these compounds by any other acid at ordinary temperature. All the normal sulphates, except lead, mercurous, barium, strontium, and calcium sulphates, are readily soluble in water. Sodium sulphate or magnesium sulphate may conveniently be used for the reactions.

1. *Lead acetate* precipitates white lead sulphate $PbSO_4$, which is only slightly attacked by water or dilute acids. It may be dissolved in boiling concentrate hydrochloric acid. It is easily dissolved in alkaline ammonium tartrate, made by treating the precipitate with tartaric acid and ammonia, as described in Art. **20,** 8, and from this solution the lead may be precipitated by potassium chromate.

2. *Mercurous nitrate* precipitates white mercurous sulphate Hg_2SO_4 from solutions that are not too dilute. This is much less soluble in water than calcium sulphate; hence, is precipitated from more dilute solutions.

3. *Barium chloride* precipitates white barium sulphate $BaSO_4$, which is insoluble in all dilute, and but slightly attacked by concentrate, acids. The presence of concentrate acids, and of some salts, hinders the immediate formation of the precipitate in very dilute solutions.

4. Some sulphates, when very highly heated in a glass tube, give off sulphurous oxide SO_2, which is recognized by its penetrating odor.

5. All sulphates in the solid form, when mixed with sodium carbonate and fused on the charcoal before the blowpipe, are reduced to sulphides by the action of the carbon, and the sulphur, or part of it, unites with the sodium, forming sodium sulphide. If, after cooling, this mass is removed

to a silver coin, or other piece of silver, broken up, and a drop of water added, the solution of sodium sulphide will attack the silver almost immediately, leaving a dark stain of silver sulphide Ag_2S.

This is not characteristic of sulphuric acid, but merely shows the presence of sulphur. The other acids of sulphur give the same reaction. It is very important, however, as it shows that the compound is a salt of one of the acids of sulphur. It is generally spoken of as the *coin test*.

THIOSULPHURIC ACID.

115. Thiosulphuric acid $H_2S_2O_3$ does not exist in the free state, but its salts, the thiosulphates, which are often erroneously called hyposulphites, are stable, and some of them are important. Most of them are soluble in water. Sodium thiosulphate may be used for the reactions.

1. *Silver nitrate* precipitates white silver thiosulphate $Ag_2S_2O_3$, which changes rapidly to yellow, then brown, and finally to black, owing to the formation of silver sulphide Ag_2S. The precipitate is easily soluble in excess of the thiosulphate.

2. *Lead acetate* precipitates white lead thiosulphate PbS_2O_3, which is soluble in nitric acid.

3. *Barium chloride* precipitates white barium thiosulphate BaS_2O_4 from rather strong solutions. It is decomposed by hydrochloric acid, giving off sulphur dioxide, and throwing out free sulphur in the solution, which it gives a yellowish appearance. The precipitate is slightly soluble in water, so in very dilute solutions no precipitate is formed.

4. *Ferric chloride* imparts a characteristic reddish-violet color to solutions of thiosulphates. The color is not permanent, but, upon standing, ferrous chloride is formed, and the solution becomes colorless.

5. All thiosulphates are decomposed by hydrochloric or sulphuric acid, giving sulphur dioxide and free sulphur. The sulphur thrown out from thiosulphates is yellow, while that from sulphites and sulphides is nearly always white.

6. Thiosulphates give the *coin test* the same as sulphates.

SULPHUROUS ACID.

116. Sulphurous acid H_2SO_3 is a weak, rather unstable acid, and its salts are also rather unstable. The sulphites of the alkalies are soluble in water, but the other sulphites are only soluble with difficulty, or are insoluble. The sulphites, especially in solution, when exposed to the air, are oxidized to sulphates; hence, we generally find sulphates mixed with sulphites. Pure sodium sulphite Na_2SO_3 is a convenient salt to use for the reactions.

1. *Silver nitrate* precipitates white silver sulphite Ag_2SO_3, which, upon standing, is decomposed into sulphuric acid and metallic silver. This action is hastened by heating.

2. *Lead acetate* precipitates white lead sulphite $PbSO_3$, which is dissolved by nitric acid.

3. *Barium chloride* precipitates white barium sulphite $BaSO_3$ from neutral sulphite solutions. This is soluble in hydrochloric acid; but, as sulphates are nearly always present in sulphites, an insoluble residue of barium sulphate generally remains. By filtering off this residue and adding a few drops of concentrate nitric acid or chlorine water to the clear filtrate, the sulphite will be oxidized to sulphate, and barium sulphate will be precipitated. If this succeeds, it shows that the solution contained sulphite. The oxidation and consequent precipitation is aided by heating.

Barium chloride does not precipitate free sulphurous acid.

4. All sulphites are easily decomposed by strong acids, yielding sulphur dioxide. They are oxidized to sulphates by chlorine or bromine water, and, like all other sulphur compounds, give the coin test.

HYDROSULPHURIC ACID.

117. Hydrogen sulphide H_2S is a weak, unstable acid, and on account of its acid properties is sometimes called *hydrosulphuric acid.* It unites with bases, as we have seen, to form sulphides. The sulphides of the alkalies and alkaline earths are soluble in water. All the others are insoluble. Sodium or ammonium sulphide may be used for the

wet reactions, and any sulphide that has been powdered may be used for the dry ones.

1. *Silver nitrate* precipitates black silver sulphide Ag_2S, which is soluble in warm nitric acid.

2. *Lead acetate* precipitates black lead sulphide PbS, which is soluble in warm nitric acid.

3. *Mercurous nitrate* precipitates black mercuric sulphide HgS, which is not dissolved by any single acid, but is soluble in aqua regia. When treated as directed in Art. **23,** 5, this precipitate is changed to a white, insoluble compound by nitric acid.

4. Nearly all the sulphides, either in the solid form or in solution, are decomposed by heating with concentrate sulphuric acid, yielding hydrogen sulphide, which is readily recognized by its odor or by the black color that it imparts to a piece of filter paper moistened with lead solution.

NITRIC ACID.

118. Nitric acid HNO_3 is a strong, stable acid, and forms a large number of salts that are also stable. All the nitrates, with the exception of a few basic ones, are soluble in water; hence, we cannot use precipitation as a means of recognizing nitric acid, and must resort to other reactions. Potassium nitrate is a good salt to use for the reactions.

1. The best test for nitric acid in solution, and, in fact, the only good ordinary test, is performed by mixing about 2 cubic centimeters, of the solution to be tested, with about an equal amount of concentrate sulphuric acid in a test tube, and cooling by holding the tube in water, or by allowing water to run over the outside of it. When the solution has reached about the temperature of the room, carefully pour a solution of ferrous sulphate down the side of the inclined tube, so that the solutions do not mix, but the ferrous sulphate forms a layer on top of the other solution. If the solution contains a nitrate, a ring will be formed where the two solutions meet, which will be variously colored according to the amount of nitric acid present. If but a small

amount of nitrate is present, the ring will be light red, while if the quantity is greater, it will be brown or almost black. The color is caused by nitric oxide NO, which is set free by sulphuric acid, uniting with the ferrous sulphate, forming an unstable compound. If the tube is shaken slightly, the liquids will be mixed slightly at the points where they come in contact, and the ring becomes wider. By heating, the compound is broken up and the liquid becomes clear. At this time, if much nitrate were present, brownish vapors of nitrogen peroxide NO_2 may be seen in the upper part of the tube.

2. As nitrites give the above reaction to a certain extent, it is necessary to distinguish between nitric and nitrous acids. To do this, place a small quantity of the solution in a test tube, and add about half the volume of dilute sulphuric acid, and small amounts of potassium-iodide solution and starch paste. If nitric acid or a nitrate alone is present, no reaction takes place. Now add a little metallic zinc. The hydrogen generated by the action of the sulphuric acid on the zinc, reduces the nitric acid to nitrous acid; this sets free the iodine, which unites with the starch, forming blue starch iodide. If nitrous acid is present, the blue color will be produced at once when the reagents are added.

3. All nitrates are decomposed by heat. The nitrates of the alkalies give off oxygen and are converted into nitrites at first, but are changed to oxides at a higher temperature. The nitrates of the heavy metals give off oxygen and nitric peroxide at once, and are converted into the oxides of these metals. If the nitrates are ignited in a small glass tube that is closed at one end, the oxygen given off will ignite a spark held at the mouth of the tube.

PHOSPHORIC ACID.

119. The phosphates of the alkalies are soluble in water. Nearly all the others are insoluble. A solution of sodium phosphate may be used for the reactions.

1. *Silver nitrate* precipitates light-yellow silver phosphate Ag_3PO_4, which is soluble in nitric acid and in ammonia.

2. *Lead acetate* precipitates white lead phosphate $Pb_3(PO_4)_2$, which is soluble in nitric acid, but insoluble in acetic acid.

3. *Barium chloride* precipitates white barium phosphate $Ba_3(PO_4)_2$, which is soluble in nitric or hydrochloric acid.

4. *Magnesium sulphate* precipitates white magnesium-ammonium phosphate $MgNH_4PO_4$ from solutions of phosphates containing ammonia and ammonium chloride. In order to avoid mistaking magnesium hydrate for magnesium phosphate, it is best to add an excess of ammonium hydrate to the magnesium sulphate, and then just enough ammonium chloride to dissolve the precipitate thus formed. To this solution add some of the solution to be tested, and shake well. In case of dilute solutions, the precipitate is not formed at once, so it should be allowed to stand for some time. Agitation aids the formation of the precipitate.

5. *Ammonium molybdate* in nitric-acid solution, when added in excess to a solution of phosphoric acid or a phosphate, produces a yellow precipitate of ammonium phosphomolybdate, which varies in composition according to conditions. It is soluble in ammonia, and also in phosphoric acid or phosphates; hence, no precipitate is formed unless there is an excess of ammonium molybdate. The best way to make this test is to place about 2 cubic centimeters of the molybdate solution in a test tube, heat it almost to boiling, and add 2 or 3 drops of the solution to be examined. If phosphoric acid is present in any considerable amount, the yellow precipitate is formed almost at once in this hot solution. Shaking also hastens precipitation. Arsenates also give a yellow precipitate in hot solutions, and silicates sometimes give a yellow color to the solution. But neither arsenates nor silicates are so readily precipitated as are phosphates, and they are easily distinguished by other reactions.

CARBONIC ACID.

120. Carbonic acid H_2CO_3 is a weak acid that has never been obtained in the uncombined state, except in very dilute aqueous solution. Its anhydride, carbon dioxide, and its

salts, the carbonates, are common, and many of the salts are important. The carbonates of the alkalies are soluble in water. All other normal carbonates are insoluble in water. Sodium carbonate is the most convenient salt to use for the reactions.

1. *Silver nitrate* precipitates white silver carbonate Ag_2CO_3, which changes to brown silver oxide Ag_2O upon boiling.

2. *Lead acetate* precipitates white lead carbonate $PbCO_3$, which is soluble in nitric acid, and also in acetic acid.

3. *Barium chloride* precipitates white barium carbonate $BaCO_3$, which is easily soluble, with effervescence, in hydrochloric acid.

4. All carbonates, either in the solid state or in solutions that are not too dilute, are decomposed by dilute hydrochloric acid, with effervescence, due to the escaping carbon dioxide. A drop of barium hydrate on a glass rod, held at the mouth of the tube where the gas is escaping, will become turbid, owing to the formation of white barium carbonate.

CHROMIC ACID.

121. Chromic acid H_2CrO_4 forms a large number of salts, known as chromates. They are all colored compounds, and are generally either yellow or red. The chromates of the alkalies are soluble in water, while most of the other chromates are insoluble. Potassium chromate serves well for the reactions.

1. *Silver nitrate* precipitates red silver chromate Ag_2CrO_4, which is soluble in either nitric acid or ammonia.

2. *Lead acetate* precipitates yellow lead chromate $PbCrO_4$, which is soluble in sodium hydrate, and is reprecipitated from this solution by nitric acid.

3. *Mercurous nitrate* precipitates red basic mercurous chromate, which is insoluble in sodium hydrate, but is dissolved by nitric acid.

4. *Barium chloride* precipitates yellow barium chromate

$BaCrO_4$, which is soluble in nitric or hydrochloric acid, and also in chromic acid.

5. Many of the dry chromates, when heated with concentrate hydrochloric acid in a test tube, are changed into chlorides of chromium and the metal that acted as the base, and free chlorine is given off.

6. A yellow normal chromate solution may be changed to a red bichromate by adding an acid, preferably nitric acid. The red bichromate thus formed may be changed back to the yellow normal chromate by adding an excess of ammonia.

7. All chromate solutions containing an excess of hydrochloric acid are reduced to green chromium chloride by heating with sulphurous acid or alcohol. Sulphuric acid serves instead of hydrochloric acid, and solutions in nitric acid can be reduced, though with difficulty.

It is sometimes necessary to reduce chromates of the heavy metals and put the solution thus obtained through the group separations in order to be sure of the results obtained in the dry way.

The chromate is dissolved in an acid that does not precipitate the metal acting as the base, alcohol is added, and the solution is boiled until it becomes a deep green and all alcohol is expelled, which may be determined by the odor. The solution is now diluted to the proper extent and put through the group separations. The chromium, which has been reduced to chromium chloride $CrCl_3$, if hydrochloric acid was used, or chromium sulphate if sulphuric acid was the solvent, will, of course, be precipitated in the third group, while the metal that acted as a base will be precipitated in the group to which it belongs.

8. If insoluble chromates are fused with sodium carbonate to which a little potassium chlorate is added, chromates of the alkalies are formed, which may be dissolved in water, while the metals of the original chromates remain as insoluble carbonates or oxides. The solution will give the reactions for chromates. Or we may dissolve the fusion in acid, reduce the solution, and proceed with the group separations as above.

COMMON ORGANIC ACIDS.

122. Salts of a few of the organic acids are among the most common substances, so the student should become familiar with them. Reactions for four of the most common are given here. If the student becomes thoroughly familiar with these, he will have no trouble in determining the others, if called upon to do so, by following the directions given for their recognition, under the less common acids.

HYDROCYANIC ACID.

123. Hydrocyanic acid HCN is a weak acid that scarcely reddens litmus paper, and its soluble salts have an alkaline reaction. The cyanides of the alkalies and alkaline earths, and mercuric cyanide, are soluble in water. All other single cyanides are insoluble. The acid and its salts are exceedingly poisonous, and should be handled with great care. Potassium cyanide may be used for the reactions.

1. *Silver nitrate* precipitates white silver cyanide $AgCN$, which is soluble in potassium cyanide; hence, no precipitate is formed until silver nitrate is present in excess. The precipitate is soluble in ammonia, and is reprecipitated from this solution by nitric acid.

2. *Lead acetate* precipitates white lead cyanide $Pb(CN)_2$, which is soluble in warm nitric acid.

3. Mix about 2 cubic centimeters of any cyanide solution, about $\frac{1}{2}$ cubic centimeter of ferrous sulphate, and 2 or 3 drops of ferric chloride, in a test tube; add sodium hydrate until the mixture is alkaline, and heat almost to boiling. Now add hydrochloric acid till the solution gives an acid reaction, and a deep-blue precipitate will be formed if the solution contains much cyanide. If the solution is very dilute, a blue coloration will be seen.

4. All cyanides are decomposed, without charring, by heating in a test tube with concentrate sulphuric acid, when

they may be recognized by their characteristic odor, which is similar to that of bitter almonds.

5. Solid cyanides, when heated in the closed tube, decompose without charring.

ACETIC ACID.

124. Acetic acid $C_2H_4O_2$ has a sharp, acid taste, and strong, disagreeable odor, by which it is readily recognized even in dilute solutions. Its salts, the acetates, are nearly all soluble in water. Sodium acetate is a convenient salt to use for the reactions.

1. *Silver nitrate* precipitates white silver acetate $AgC_2H_3O_2$ from rather strong solutions of neutral acetates, or from strong solutions of the acid. This precipitate is dissolved rather easily in water and more readily in ammonia.

2. *Mercurous nitrate* precipitates white mercurous acetate $Hg_2(C_2H_3O_2)_2$ from neutral solutions of acetates that are not too dilute, and from strong solutions of the free acid. The precipitate is somewhat soluble in cold water, and is more readily dissolved if the water is warm. It is also soluble in excess of the reagent.

3. *Ferric chloride* colors a neutral acetate solution red, owing to the formation of ferric acetate $Fe(C_2H_3O_2)_3$. Upon boiling, the iron is precipitated as brown basic acetate $Fe(OH)_2(C_2H_3O_2)$, which settles and leaves the supernatant liquid clear.

If the ferric chloride is added to an acetic-acid solution a faint red color is seen, which becomes deeper upon the addition of ammonia. If enough ammonia is added to just neutralize the solution, and this is heated, the same reaction is obtained as with neutral acetates.

4. Any acetate heated with concentrate sulphuric acid, is decomposed, giving off free acetic acid, which is recognized by its odor. If we modify this by adding concentrate sulphuric acid and a little alcohol, and heating, acetic ether is formed during the decomposition. This is recognized by its pleasant odor. In either case, the acetate does not char, as a rule, and never to any great extent.

5. Solid acetates when heated in the closed tube are decomposed without charring, yielding acetone, which may be recognized by its odor, and leaving the oxide or carbonate of the metal in the tube. In cases where the oxide of the metal remains, carbon dioxide also escapes; and in case of some of the weak bases some free acetic acid is driven off.

TARTARIC ACID.

125. Tartaric acid $C_4H_6O_6$ is a colorless, crystalline solid, with rather a pleasant acid taste. It dissolves quite readily in water. Tartrates of the alkali metals, and a few others, are soluble in water. Those that are insoluble in water are easily dissolved by nitric or hydrochloric acid. Sodium-potassium tartrate may be used for the reactions.

1. *Silver nitrate* gives no precipitate with free tartaric acid, but in neutral solutions of tartrates it precipitates white silver tartrate $Ag_2C_4H_4O_6$, which is dissolved by either nitric acid or ammonia. Boiling decomposes the precipitate, and deposits black metallic silver.

2. *Lead acetate* precipitates white lead tartrate $PbC_4H_4O_6$ from solutions of tartaric acid or tartrates. It dissolves easily in nitric acid or ammonia.

3. *Barium chloride* precipitates white barium tartrate $BaC_4H_4O_6$ when added in excess. The precipitate is soluble in nitric, hydrochloric, or acetic acid.

4. When tartaric acid or a tartrate in the solid state is heated with concentrate sulphuric acid, it chars, owing to the separation of carbon, and carbon monoxide is given off. A characteristic odor like that of burned sugar may be noted.

5. Solid tartaric acid and tartrates, when heated in the closed tube, char and give off the characteristic odor resembling that of burned sugar. A black residue of carbon is left in the tube, mixed with the carbonate of the metal, if the substance was a tartrate.

OXALIC ACID.

126. Oxalic acid $C_2H_2O_4$ in the dry state is a white powder. With 2 molecules of water it forms colorless crystals. In either form it dissolves readily in water. The oxalates of the alkalies are soluble, while most of the others are insoluble in water. Ammonium oxalate is common, and serves well for the reactions.

1. *Silver nitrate* precipitates white silver oxalate $Ag_2C_2O_4$, which is readily dissolved by ammonia, or hot concentrate nitric acid. It is dissolved with some difficulty in dilute nitric acid.

2. *Barium chloride* precipitates white barium oxalate BaC_2O_4 from neutral solutions of oxalates. The precipitate is easily dissolved by hydrochloric or nitric acid, and less easily in acetic or oxalic acid, or ammonium chloride, and is slightly soluble in water. Ammonia reprecipitates it from its solutions in nitric or hydrochloric acid.

3. *Calcium chloride*, or any other neutral calcium solution, precipitates white calcium oxalate CaC_2O_4 from even very dilute solutions of oxalates or oxalic acid. The precipitate is almost insoluble in water, and is only very slightly soluble in acetic or oxalic acid, but is easily dissolved in nitric or hydrochloric acid. In very dilute solutions, the precipitate is formed slowly, but is promoted by heating and by the addition of ammonia.

4. Oxalic acid, and all oxalates in the dry state, when heated with concentrate sulphuric acid, are decomposed without charring. The sulphuric acid takes water from them, and carbon monoxide and carbon dioxide are given off. The carbon monoxide may be ignited at the mouth of the tube, and burns with a blue flame, either at the mouth, or down in the tube, depending upon the amount that is given off. The carbon dioxide precipitates the barium from a drop of barium hydrate held at the mouth of the tube on a glass rod, and thus renders it turbid. The student should never fail to get the tests for these two gases, as this is the most characteristic reaction for oxalic acid.

5. In the closed tube the oxalates are all decomposed at

a red heat. If heated carefully, they do not char if pure. Oxalic acid is decomposed into carbon monoxide, carbon dioxide, and water. The oxalates of the alkalies, and of barium, strontium, and calcium, are decomposed into carbon monoxide and carbonates of the metals. The other oxalates give off both carbon monoxide and carbon dioxide, and are reduced to the oxides or to the metallic state, according to the ease with which they are reduced. The carbon monoxide may be ignited, and burns with a blue flame.

127. Remarks.—The four acids given are the most common and important of the organic acids, and if the student makes himself familiar with these, he will experience no difficulty in determining others, should he be called upon to do so.

It will be noted that heating with concentrate sulphuric acid is the most characteristic test for these acids. After a little experience they may be determined with certainty by this reaction alone; but the result thus obtained should always be confirmed by making use of the other reactions given. The reactions for arsenious and arsenic acids, which are quite common, have been given with the reactions for the metals where they are usually found in the course of analysis.

LESS COMMON INORGANIC ACIDS.

BORIC ACID.

128. Boric acid H_3BO_3 is rather weak in all its chemical relations. It is soluble in water, and the solution reddens litmus. It forms but a limited number of salts, and of these, sodium biborate (borax) is the only very important one. The salts of the alkalies are the only ones that are readily soluble in water. Solutions of all the soluble borates in water give an alkaline reaction.

1. *Silver nitrate*, when added to a concentrate solution of a normal borate of an alkali metal, gives a white precipitate of $2AgBO_2, H_2O$, which has more or less of a yellow tint, owing to the formation of a small quantity of silver

oxide Ag_2O. In concentrate solutions of the acid borates, it gives a white precipitate of $Ag_6B_8O_{15}$. From dilute solutions of the borates of the alkalies, brown silver oxide Ag_2O is precipitated. All of these precipitates are soluble in nitric acid or ammonia.

2. *Lead acetate* precipitates white lead metaborate $Pb(BO_2)_2$ from strong solutions. The precipitate is soluble in an excess of the reagent.

3. *Barium chloride* precipitates white barium metaborate $Ba(BO_2)_2$ from strong solutions of normal borates. In acid borates, the precipitate produced is $Ba_3B_{10}O_{18}$, which is also white. Either precipitate is soluble in an excess of the reagent, in ammonium salts, and in acids.

4. The best, and, in fact, the only reliable, test for boric acid or borates is the characteristic green flame. If boric acid is mixed with alcohol, and the latter ignited, the boric acid will impart a green color to the flame at once; but the borates are not volatile, and, consequently, do not color the flame until we get the boric acid in a volatile form. To do this, mix, in a porcelain dish, a little of the borate to be tested with concentrate sulphuric acid; add some alcohol, heat the contents of the dish, and ignite the alcohol. The sulphuric acid sets boric acid free, and this colors the flame. Boric acid does not usually appear to color the whole flame, but gives to the flame a green border. The delicacy of the reaction is increased by stirring the contents of the dish.

5. If a borate is ground up with a mixture containing about twice its bulk of acid potassium sulphate and about half its bulk of calcium fluoride, a drop or two of water added to form a paste, and this paste held on a platinum wire in the flame of a Bunsen burner, it gives the flame a green color for a moment.

CHLORIC ACID.

129. Chloric acid $HClO_3$, in very concentrate solution, is a slightly yellowish liquid, having an odor similar to that of nitric acid. More dilute solutions are colorless and

odorless. All the chlorates are soluble in water; so no precipitates are obtained.

1. When solutions of chlorates are heated in a test tube with concentrate hydrochloric acid, the liquid assumes a greenish-yellow color, and greenish-yellow vapors of chlorine tetroxide and free chlorine escape.

2. If a solution of a chlorate is colored light blue by a solution of indigo in sulphuric acid, by adding a little dilute sulphuric acid, and then carefully introducing a few drops of a solution of sodium sulphite, the solution is decolorized. The sulphurous acid of the sulphite takes oxygen from the chlorate, setting free chlorine, or a lower oxide of it, which destroys the color of the indigo.

3. Chlorates, when gently heated with concentrate sulphuric acid, are decomposed, yielding greenish-yellow explosive fumes of chlorine tetroxide Cl_2O_4. Great care must be taken in performing this operation, as the chlorine tetroxide explodes violently at a moderate temperature, often throwing the acid some distance. Very small quantities should be used, and the tube should always be held pointing away from the operator.

4. Nearly all chlorates, when heated in the closed tube, give off oxygen, and are reduced to chlorides. The oxygen will ignite a spark held at the mouth of the tube. The chlorates of barium, strontium, and calcium give off both oxygen and chlorine, and are reduced to oxides.

HYPOCHLOROUS ACID.

130. Hypochlorous acid $HClO$ and the hypochlorites are very unstable. Hypochlorous acid has never been obtained, except in solution, but its salts are known, and calcium hypochlorite, known as chloride of lime, or bleaching powder, is important.

1. *Silver nitrate* precipitates white silver chloride $AgCl$ from solutions of calcium hypochlorite, to which enough nitric acid has been added so that it does not emit an odor

of chlorine. Silver hypochlorite is formed at first, but this decomposes into silver chloride and silver chlorate almost immediately.

2. *Lead acetate* precipitates white lead chloride $PbCl_2$, which soon decomposes, forming oxides of lead, giving the precipitate a yellow color that gradually grows darker until it becomes brown, owing to the formation of lead dioxide.

3. When hydrochlorites are treated with concentrate sulphuric or hydrochloric acid, they are decomposed, giving off free chlorine, which may be recognized by its color and odor.

HYDROFLUORIC ACID.

131. Hydrofluoric acid HF is a colorless, corrosive liquid with a penetrating odor. It fumes strongly in the air, and attacks the tissues, causing sores that are difficult to heal. It is distinguished from all other acids by its power of decomposing silica and silicates that are insoluble in other acids. The fluorides are stable compounds. Those of the alkalies are quite readily dissolved by water, while all the others are either insoluble or are dissolved with more or less difficulty.

1. *Silver nitrate* precipitates white silver fluoride AgF from rather strong solutions. It is somewhat soluble in water, and easily dissolved by nitric acid, but is insoluble in ammonia.

2. *Lead acetate* precipitates white lead fluoride PbF_2, which is almost insoluble in water, but is dissolved by nitric acid.

3. *Barium chloride* precipitates white barium fluoride BaF_2 from solutions of hydrofluoric acid, but much more readily from solutions of fluorides. The precipitate is almost absolutely insoluble in water, but is dissolved by hydrochloric or nitric acid.

4. *Calcium chloride* precipitates white calcium fluoride CaF_2, which is so transparent that it is often difficult to see the precipitate at first. It is almost absolutely insoluble in water and is only slightly attacked by acids in the cold. Hot

concentrate hydrochloric acid dissolves it more readily, but only with great difficulty.

5. Nearly all fluorides are decomposed by warm concentrate sulphuric acid, yielding hydrofluoric acid in the gaseous state. If a fluoride is heated with concentrate sulphuric acid in a platinum crucible, covered with a piece of glass, coated with wax through which lines are traced so that the hydrofluoric acid can come in contact with the glass, it attacks the silicon of the glass, forming the volatile fluoride of silicon SiF_4, and thus etches the glass. After removing the wax, the lines may be plainly seen.

6. A characteristic test for a fluoride may be made by mixing about equal parts of the finely ground fluoride, and powdered silicon dioxide SiO_2. Place this mixture in a test tube and add about twice its volume of concentrate sulphuric acid. Fit the test tube with a perforated rubber stopper, through which a bent delivery tube passes, as shown in Fig. 9.

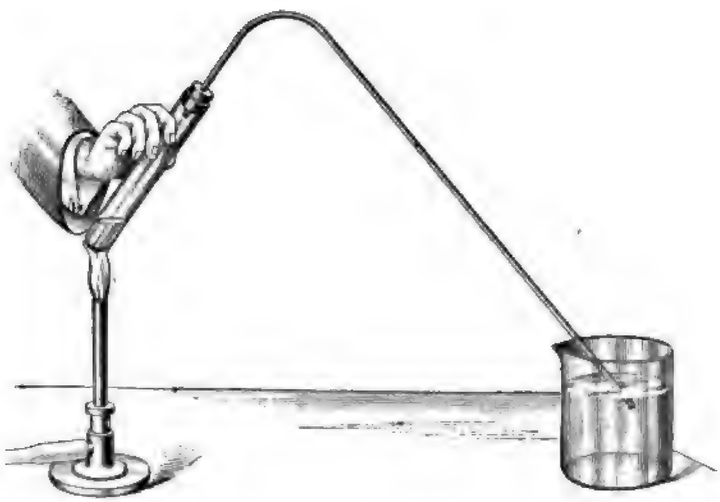

FIG. 9.

The contents of the test tube are now heated, while the end of the delivery tube is held under water. The volatile fluoride of silicon SiF_4 that is formed passes through the delivery

tube into the water, where it produces a white, gelatinous precipitate of silicic acid. At the end of the operation, first remove the delivery tube from the water, then withdraw the stopper from the test tube, and finally remove the test tube from the flame.

Great care must be taken in performing this experiment. Water must not be allowed to come in contact with the hot sulphuric acid or it will cause an explosion, and the hot acid that will be spattered about may cause much damage. The operation must not be continued too long, or the hydrofluoric acid may dissolve the bottom out of the test tube.

SILICIC ACID.

132. Silicic acid H_4SiO_4 is a gelatinous substance that may be obtained in dilute aqueous solution, from which it shows a great tendency to separate as a gelatinous precipitate. It is a very weak acid in its chemical relations, and will scarcely color litmus paper. The silicates of the alkalies are soluble, but all other silicates are insoluble in water. Some of the silicates are soluble in acids, while others are almost entirely insoluble. Silicic acid and the silicates are not frequently met except in mineral analysis, where they are very common. Most of the silicates are represented by formulas that express their derivation from metasilicic or polysilicic acids, but the reactions are the same for these as for the normal silicic acid.

1. *Lead acetate* precipitates white lead silicate from solutions of the alkali silicates. The precipitate is soluble in nitric acid.

2. *Barium chloride* precipitates white barium silicate from solutions of the silicates of the alkalies. The precipitate is soluble in nitric or hydrochloric acid.

3. *Concentrate hydrochloric acid* precipitates white, gelatinous silicic acid from rather strong solutions of the alkali silicates. If the solution is weak, the precipitate only appears after standing some time, or on being concentrated.

4. *Ammonium-molybdate* solution, when heated with a solution of a silicate, gives the solution a yellow color; and, if the silicate solution is strong, a slight yellow precipitate may be formed.

5. All silicates, when fused with sodium carbonate, yield carbonates of the metal and sodium silicate. The sodium silicate may be dissolved in water, while the carbonate of the metal remains undissolved, or the metallic carbonates may be dissolved in hydrochloric acid, while the silicic acid is partially precipitated. The silicic acid is somewhat soluble in water, but by removing it, or evaporating to dryness and heating, water is driven off, and there is left silicic oxide SiO_2, which is insoluble in water and all acids except hydrofluoric acid.

If this silicic oxide is separated from the metals by filtration or decantation, and heated in a lead or plantinum dish with a concentrate solution of hydrofluoric acid, it will be dissolved, forming volatile silicon tetrafluoride, which will be driven off by the heat, leaving nothing in the dish except traces of metallic compounds that were not perfectly separated from the silicic oxide.

6. A very convenient test for a silicate depends upon the formation of what is known as the *silica skeleton*, in the *microcosmic bead*. A bead is made of microcosmic salt (hydrogen-sodium-ammonium phosphate) in the same manner that a borax bead is made; a little of the silicate is added, and the bead is brought into the hottest part of the blowpipe flame. The metals form part of the fused portion of the bead, while the silicic oxide (silica) remains undissolved and floats in the bead. The bead is sometimes colored with a little copper sulphate, to make the skeleton more easily seen.

NITROUS ACID.

133. Nitrous acid HNO_2 is a blue, unstable liquid that decomposes into nitric acid, nitrous oxide, and water, at ordinary temperatures. It may be preserved at very low

temperatures. Its salts, the nitrites, are also rather unstable. Most of them are soluble in water.

1. *Silver nitrate* gives a white precipitate in rather strong solutions of the alkali nitrites. The precipitate is slightly soluble in cold water, and is much more easily dissolved if the water is heated.

2. *Ferrous sulphate* produces a slight yellowish or greenish-yellow coloration in neutral nitrite solutions. This is changed to a deep-brown color upon the addition of acetic acid. If the ferrous sulphate contains free sulphuric acid, the brown color is produced at once.

3. If a few drops of a mixture of potassium iodide, starch paste, and dilute sulphuric acid, are added to a solution of a nitrite, a deep-blue color is immediately produced, owing to the formation of blue starch iodide. This is a very delicate reaction when properly handled, and shows the presence of nitrites in even very dilute solutions. The potassium iodide must be free from iodate, and the mixture of potassium iodide, starch, and sulphuric acid must remain colorless until added to the nitrite solution, or the reaction shows nothing. The sulphuric acid may be considerably diluted if necessary.

4. Nitrites, when heated with concentrate sulphuric or hydrochloric acid, are decomposed, and brownish-red fumes of nitric oxide are given off.

HYDROSULPHOCYANIC ACID.

134. Hydrosulphocyanic acid *HSCN*, or *hydrothiocyanic acid*, as it is also called, is an oily liquid with a penetrating odor, somewhat similar to that of acetic acid. It mixes with water, forming a very poisonous liquid with an acid reaction. Upon standing, it is gradually dissociated, and hydrocyanic acid is formed during the decomposition. It unites with all bases, forming sulphocyanides, all of which are soluble in water, except those of silver, lead, and mercury.

1. *Silver nitrate* precipitates white, curdy silver sulpho-

cyanide $AgSCN$, which is insoluble in dilute nitric acid, but is soluble in ammonia.

2. *Lead acetate* precipitates yellowish lead sulphocyanide $Pb(SCN)_2$, which is changed to a white basic compound by boiling.

3. *Mercurous nitrate* gives a white precipitate of mercurous sulphocyanide $Hg_2(SCN)_2$, or a gray precipitate of mercuric sulphocyanide $Hg(SCN)_2$ and free mercury, depending upon the degree of concentration and the proportions in which the two liquids are mixed. The white mercurous sulphocyanide may be changed to the gray precipitate of mercuric sulphocyanide and mercury by boiling.

4. *Copper sulphate* precipitates greenish-black copper sulphocyanide $Cu(SCN)_2$ from strong solutions of the alkali sulphocyanides. In dilute solutions, it produces an emerald-green coloration, but no precipitate.

5. *Ferric-chloride* solution, acidulated with hydrochloric acid, imparts a blood-red color to solutions of sulphocyanides, but does not produce a precipitate. The color is due to the formation of red, soluble ferric sulphocyanide $Fe(SCN)_3$. The color is not injured by hydrochloric acid, but is destroyed by mercuric chloride.

6. When a sulphocyanide is heated with nitric acid, a violent decomposition takes place, during which nitric and carbonic oxides are given off, and sulphuric acid is formed.

HYDROFERROCYANIC ACID.

135. Hydroferrocyanic acid $H_4Fe(CN)_6$ is a colorless, crystalline substance that readily dissolves in water, giving a liquid with a strong acid reaction. The ferrocyanides of the alkalies and alkaline earths are soluble, while most of the others are insoluble in water. They are all decomposed by ignition in the closed tube, and if they are not quite dry, hydrocyanic acid, carbon dioxide, and ammonia are given off. If perfectly dry, nitrogen, and sometimes cyanogen, escape.

1. *Silver nitrate* precipitates white silver ferrocyanide $Ag_4Fe(CN)_6$, which is insoluble in nitric acid, and in ammonia in the cold, but is dissolved by potassium cyanide.

2. *Lead acetate* precipitates white lead ferrocyanide, which has the formula $Pb_2Fe(CN)_6$, and is not dissolved by dilute nitric acid.

3. *Copper sulphate* precipitates reddish-brown copper ferrocyanide $Cu_2Fe(CN)_6$, which is insoluble in dilute acids.

4. *Ferric chloride* precipitates dark-blue ferric ferrocyanide $Fe_4'''Fe_3''(CN)_{18}$, which is insoluble in dilute mineral acids, but may be dissolved in a large excess of potassium ferrocyanide, giving a deep-blue solution. The precipitate is known as *Prussian blue.*

5. If Prussian blue is heated with an ammoniacal solution of silver, ferric oxide is precipitated, and silver cyanide is formed, and remains in solution. If the ferric oxide is separated, and the solution acidified with nitric acid, white silver cyanide is thrown down.

6. All solid ferrocyanides, when heated with 1 part of water and 3 or 4 parts of concentrate sulphuric acid, are decomposed, yielding hydrocyanic acid, which may be recognized by its odor.

HYDROFERRICYANIC ACID.

136. Hydroferricyanic acid $H_3Fe(CN)_6$ is soluble in water, and many of its salts are also soluble. The ferricyanides, like the ferrocyanides, are all decomposed upon ignition in a closed tube, and in a similar manner.

1. *Silver nitrate* precipitates orange or reddish-brown silver ferricyanide $Ag_3Fe(CN)_6$, which is insoluble in nitric acid, but is dissolved by ammonia or potassium cyanide.

2. *Copper sulphate* precipitates yellowish-green copper ferricyanide $Cu_3Fe_2(CN)_{12}$, which is insoluble in dilute hydrochloric acid.

3. *Ferric chloride* does not produce a precipitate in pure ferricyanide solutions, but gives the solution a dark coloration;

but as ferricyanides often contain ferrocyanides, a precipitate is frequently obtained that is due to impurity. A precipitate will also be formed if the ferric chloride contains ferrous compounds.

4. *Ferrous sulphate* precipitates blue ferrous ferricyanide $Fe_3''Fe_2'''(CN)_{12}$, which is insoluble in dilute inorganic acids. The precipitate is known as *Turnbull's blue.*

5. All ferricyanides are decomposed when heated with 1 part of water and 3 parts of concentrate sulphuric acid, and yield hydrocyanic acid, in the same manner that the ferrocyanides do.*

HYDROFLUOSILICIC ACID.

137. Hydrofluosilicic acid H_2SiF_6 is a white, deliquescent substance that readily dissolves in water, forming a strongly acid liquid. It may be obtained by leading silicon tetrafluoride SiF_4 into water, when hydrofluosilicic and silicic acids are formed. Its salts are called silicofluorides. Most of them are soluble in water.

1. *Lead acetate*, when added in excess to hydrofluosilicic acid or a silicofluoride solution, gives a white precipitate of lead silicofluoride $PbSiF_6$.

2. *Barium chloride* precipitates white barium silicofluoride $BaSiF_6$, which is insoluble in dilute acids.

3. *Ammonium hydrate* added in excess to solutions of hydrofluosilicic acid or its salts, decomposes them, forming insoluble silicic and soluble ammonium fluoride.

4. All solid silicofluorides, when heated with concentrate sulphuric acid, are decomposed with the evolution of silicon tetrafluoride and hydrofluoric acid. If a drop of water on a glass rod is held at the mouth of the tube, it becomes turbid, owing to the formation of silicic acid. Care must be taken

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* It will be noticed that hydrocyanic acid was treated as an organic acid, while the other cyanogen acids are treated among the inorganic acids. This is largely an arbitrary division, as all these acids are allied to both organic and inorganic compounds. Hydrocyanic acid seems to have more organic than inorganic properties, while in the other acids the inorganic properties appear to predominate.

not to let the water come in contact with the hot sulphuric acid, and if the operation is performed in a test tube, it must not be continued too long or the hydrofluoric acid may dissolve the tube.

LESS COMMON ORGANIC ACIDS.

CITRIC ACID.

138. Citric acid $C_6H_8O_7$ is obtained in colorless crystals having 1 molecule of water. It dissolves in water readily, forming a liquid with a pleasant acid taste. The citrates of the alkalies, and a number of others, are soluble in water.

1. *Silver nitrate* precipitates white silver citrate $Ag_3C_6H_5O_7$ from solutions of the normal citrates of the alkalies. If rather a large quantity of this precipitate is boiled with a small amount of water, it is decomposed with the separation of metallic silver.

2. *Lead acetate*, when added in excess to a solution of citric acid or a citrate, precipitates white lead citrate $Pb_3(C_6H_5O_7)_2$, which is soluble in ammonia that is free from carbonate.

3. *Barium hydrate*, added in excess to a rather strong citric acid solution, precipitates white barium citrate $Ba(C_6H_5O_7)_2$. As this precipitate is somewhat soluble in water, it is not obtained in dilute solutions.

4. Mix about equal parts of citric acid and glycerine, and heat gently until the mixture begins to puff up. Dissolve this mass in ammonia, evaporate off the excess, and add 2 or 3 drops of a solution, consisting of 1 part of red, fuming nitric acid and 4 parts of water. The solution assumes a green color, which is changed to blue by gently heating. A drop or two of hydrogen peroxide may be used instead of nitric acid. This reaction may be used to detect small quantities of citric acid in the presence of oxalic, tartaric, and malic acids.

5. Citric acid, and all citrates in the solid state, when

heated with concentrate sulphuric acid, are decomposed, yielding, at first, carbon monoxide, then carbon dioxide and acetone also, while the solution remains clear; finally the solution blackens, and sulphur dioxide is given off. In order to get these gases in the above order, the mixture should be heated slowly. Carbon monoxide may be recognized by its blue flame, carbon dioxide by its property of rendering turbid a drop of barium hydrate, and acetone and sulphur dioxide by their characteristic odors.

6. Citric acid and citrates, when heated in the closed tube, char, and emit pungent acid fumes that are readily distinguished from those given off by tartaric acid when it carbonizes.

7. *Calcium chloride* does not produce a precipitate in solutions of free citric acid, but if enough ammonium or sodium hydrate is added to neutralize the solution, white calcium citrate $Ca_3(C_6H_5O_7)_2$ is thrown down, provided the solution is not too dilute.

MALIC ACID.

139. Malic acid $C_4H_6O_5$ is a deliquescent, crystalline substance that readily dissolves in water. Most of the malates are also soluble in water.

1. *Silver nitrate* precipitates white silver malate $Ag_2C_4H_4O_5$ from solutions of normal malates of the alkalies. The precipitate becomes slightly gray upon standing for some time, or more readily by boiling.

2. *Lead acetate* precipitates white lead malate $PbC_4H_4O_5$ from solutions of malic acids or malates. If the solution is acid, precipitation is promoted by rendering the solution just neutral, with ammonia, but taking care to avoid an excess, for the precipitate is soluble both in malic acid and in ammonia. It is also soluble in acetic acid. If the solution, in which the precipitate is suspended, is boiled, part of the precipitate is dissolved and the rest will melt into a mass that resembles resin fused under water.

3. If calcium chloride, ammonium chloride, and ammonia are added to a solution of malic acid or a malate, no precipitate is formed even if the solution is boiled. This serves to distinguish between malic acid and citric acid.

4. *Lime water*, prepared with boiling water, gives no precipitate with malic acid or malates even upon boiling.

5. Malic acid, when heated with nitric acid, is decomposed with the evolution of carbon dioxide and formation of oxalic acid.

6. When heated in the closed tube, malic acid is decomposed into fumaric acid, water, and maleic anhydride $C_4H_2O_3$. Water and maleic anhydride are first driven off, and then the fumaric acid is volatilized and condenses upon the upper part of the tube where it is cool, forming a crystalline sublimate. This is a characteristic reaction for malic acid.

7. If a solution of malic acid in a test tube is acidified with a few drops of sulphuric acid, a little potassium bichromate added, and the contents of the tube heated to boiling, an odor resembling that of fresh apples is obtained. This reaction may be used to detect malic acid in the presence of citric acid.

8. If malic acid, or a malate in the solid form, is carefully heated with concentrate sulphuric acid, carbon monoxide and carbon dioxide are given off at first; then the acid turns brown, and finally black, and sulphur dioxide is evolved. The carbon monoxide and carbon dioxide are recognized, in the usual manner, by the blue flame and drop of barium hydrate. The sulphur dioxide is recognized by its characteristic penetrating odor.

FORMIC ACID.

140. Formic acid CH_2O_2 is a colorless, corrosive liquid that fumes slightly in the air and has a very penetrating odor. All formates are soluble in water. One of their most characteristic properties is the power of reducing compounds of the heavy metals, either to the metallic condition or to a lower state of oxidation.

1. *Silver nitrate* gives no immediate precipitate in solutions of free formic acid or dilute solutions of formates. In concentrate solutions of alkali formates, white silver formate $AgCHO_2$ is thrown down. This precipitate rapidly assumes a dark color, owing to its reduction to metallic silver. If the test of formic acid or formate that failed to give a precipitate at first, is allowed to stand, or is heated, metallic silver separates as a gray powder, or as a coating on the sides of the test tube. This reduction is prevented by an excess of ammonia.

2. *Mercurous nitrate* gives no precipitate in solutions of free formic acid, but in strong solutions of alkali formates, white glistening mercurous formate $Hg_2(CHO_2)_2$ separates. This precipitate rapidly becomes gray, owing to the reduction to metallic mercury. The precipitate is completely reduced after standing for some time in the cold, but, by heating, complete reduction is accomplished almost immediately.

3. *Mercuric chloride*, free from hydrochloric acid, when heated with a solution of formic acid or a formate, is reduced, and mercurous chloride Hg_2Cl_2 separates as a white precipitate before the solution reaches the boiling point. This reaction serves to distinguish formic from acetic acid. It is hindered or prevented by the presence of hydrochloric acid or alkali chlorides.

4. *Ferric chloride*, when added to a neutral formate solution imparts a deep-red color to the solution. The same result may be obtained by adding ferric chloride to formic acid, and then just neutralizing with ammonia. This reaction is similar to the reaction of ferric chloride with acetic acid.

5. Formic acid and all solid formates, when heated with concentrate sulphuric acid, are decomposed, the sulphuric acid extracting water, and setting free carbon monoxide, which escapes with effervescence, and, when ignited, burns with a blue flame. The solution does not carbonize, but remains clear, unless some organic impurity is present. When formates or formic acid are heated with concentrate sulphuric

acid and alcohol, ethyl formate is evolved, which is recognized by its peculiar odor, resembling that of rum.

6. All formates, when ignited in the closed tube, char, and give off carbon monoxide, which, when ignited, burns with a blue flame. In many cases carbon dioxide is also given off, which renders the ignition of the carbon monoxide difficult. Carbonates, oxides, or metals are left in the tube.

SALICYLIC ACID.

141. Salicylic acid $C_7H_6O_3$ is a colorless, odorless, crystalline substance that dissolves but slightly in cold water, more readily in hot water, and very freely in alcohol and other organic solvents. It forms two series of salts, known as normal and basic salts. Most of the normal salts are readily dissolved by water, while many of the basic salts are but slightly soluble in that medium.

1. Lead acetate precipitates *white lead salicylate* $Pb(C_7H_5O_3)_2$ from normal alkali salicylate solutions. The precipitate is soluble in an excess of lead acetate or acetic acid, but not in ammonia. It may be dissolved by heating in the solution from which it was precipitated, and, upon cooling, will separate in crystals.

2. *Ferric chloride*, in very dilute solution, when added in small amount to a water solution of salicylic acid or one of its salts, imparts a deep-violet color to the solution. This is a very characteristic reaction, but it is hindered by the presence of some other organic acids, and prevented by hydrochloric acid or ammonia.

3. If a solution of salicylic acid in methyl alcohol (wood alcohol) is heated with about half its volume of concentrate sulphuric acid, methyl salicylate is formed, which is recognized by its characteristic odor of wintergreen oil, of which it is the chief constituent. A solution of salicylic acid in ordinary alcohol, when heated with concentrate sulphuric acid, yields ethyl salicylate, which has an odor similar to that of methyl salicylate.

4. Salicylic acid, when carefully heated in a closed tube, is not decomposed, but sublimes, forming needle-shaped crystals on the cool portion of the tube. If quickly ignited at a high temperature, it is decomposed into phenol and carbon dioxide.

BENZOIC ACID.

142. Benzoic acid $C_7H_6O_2$ is a white, crystalline substance that, when strictly pure, is odorless, but generally has a faint aromatic odor, due to the presence of small quantities of impurity. It is very sparingly soluble in cold water, more freely in hot water, and dissolves readily in alcohol. Most of the benzoates are soluble in water, but a few, having weak bases, are insoluble.

1. *Lead acetate* gives no precipitate with free benzoic acid, but, from rather strong solutions of the alkali benzoates, it precipitates lead benzoate $Pb(C_7H_5O_2)_2$, which is soluble in excess of lead acetate and also in acetic acid.

2. *Ferric-chloride* solution, carefully mixed with a little very dilute ammonia until it takes on a brownish-red color, but remains clear, precipitates flesh-colored basic ferric benzoate $Fe_2(C_7H_5O_2)_6Fe_2O_3$, which is decomposed by hydrochloric acid, with separation of benzoic acid. This reaction serves to distinguish between benzoic and salicylic acids.

3. Benzoic acid is dissolved in concentrate sulphuric acid without decomposition. It is precipitated unchanged from its solution in sulphuric acid by the addition of water.

4. Strong mineral acids, when added to concentrate solutions of the soluble benzoates, take the place of the benzoic acid that is thrown out as a glistening, white powder. Benzoic acid may be obtained in the same way from insoluble benzoates, by adding an acid that forms a soluble salt with the base with which it is united.

5. Pure benzoic acid, when heated in a closed tube, volatilizes completely, leaving the tube clean; but there are

generally organic impurities present, which remain in the tube as a charred residue. The acid vapor given off has an irritating effect on the tissues, and when inhaled provokes coughing.

SYSTEMATIC EXAMINATION OF SOLUTIONS FOR ACIDS.

143. It would be a difficult matter to formulate a scheme for the detection and separation of acids in a solution, similar to the one used for the metals, which would be so complete, exact, and practical; and, fortunately, this is unnecessary, for the frequently occurring acids are few in number, and, as a rule, only one, or, at most, but two or three, will be found in any one solution. In a great majority of cases, after determining the metals in a solution—which should always be done first—enough will be known of the composition of the solution so that we may proceed at once to apply special tests for the acids. In this part of the work, more than in any of the preceding, the student must apply all his knowledge of chemistry, and consider carefully the full significance of each reaction, and of each fact which he discovers as he proceeds, or he will make much unnecessary work for himself. For instance, it would be a waste of time and chemicals to examine a neutral or acid solution, in which silver or mercurous compounds had been found, for hydrochloric, hydrobromic, or hydriodic acid, for these compounds cannot exist in such a solution in the presence of these acids. For the same reason, it would be useless to look for sulphuric acid in a solution containing barium or other metals whose sulphates are insoluble, or to examine a neutral solution containing calcium for phosphoric or oxalic acid.

All solutions should be tested with litmus paper before the analysis is commenced, or erroneous conclusions may be drawn. For instance, silver chloride may exist in ammoniacal solution, or phosphates and oxalates of the alkaline earths may exist in acid solution.

It sometimes happens that the separation of the metals

rom a solution gives no clue to the acid or acids, and it ecomes desirable to pursue a systematic course for their letection. This is accomplished by dividing them into three roups, by means of reagents. The first group is composed f those acids that are precipitated by barium chloride, the econd contains those that are not precipitated by barium hloride but are precipitated by silver nitrate, and the third roup is made up of those acids that are not precipitated by ither of these reagents. Tables 2 and 3 give the color and olubility of the precipitates produced by these reagents, and s lead acetate helps to classify the acids, a table (4) is given howing the color and solubility of precipitates produced y this reagent.

144. Preparation of the Solution.—In many cases, reparation is not required, but if the solution contains netals that would interfere with the reactions, they must be emoved by precipitation. The solution should be slightly cid; if it is alkaline or neutral, just enough nitric acid is dded to give an acid reaction with test paper. To remove he metals of the first and second groups, lead hydrogen-ulphide gas through the solution until they are all precipi-ated. Then filter and boil the filtrate until all the hydrogen ulphide is expelled. If metals of the third, fourth, and fifth roups are present, add to the solution a slight excess of odium carbonate, boil for a moment, and filter. The filtrate vill contain the acids, freed from such metals as would inter-ere with their determination. Render this slightly acid with itric acid, and boil till all carbon dioxide is expelled; then dd dilute ammonia, drop by drop, until a point is reached t which the solution does not give a reaction with either red r blue litmus paper. It is now ready to be examined for the cids. If chromic acid was present, and was reduced by the ydrogen sulphide, this fact must be noted. The solution s now divided into three equal parts. The first portion is reated with barium chloride, the second with silver nitrate, nd the third with lead acetate. The precipitates produced n each case are given in the accompanying tables.

TABLE 2.

ACIDS PRECIPITATED BY BARIUM CHLORIDE.

Acid.	Color of Precipitate.	Solubility.
Sulphuric	White.	Insoluble in HCl.
Thiosulphuric	White.	Soluble in HCl with evolution of SO_2 and free sulphur.
Sulphurous	White.	Soluble in HCl with evolution of SO_2.
Phosphoric	White.	Soluble in HCl.
Carbonic	White.	Soluble in HCl with effervescence.
Chromic	Yellow.	Soluble in HCl.
Hydrofluoric	White.	Soluble in HCl.
Boric	White (from concentrate solution).	Soluble in HCl.
Silicic	White.	Soluble in HCl.
Hydrofluosilicic	White.	Insoluble in HCl.
Oxalic	White.	Soluble in HCl.
Tartaric	White.	Soluble in HCl.

Citric and *malic* acids belong in this group, but must be recognized by special reactions.

145. Grouping the Acids.—In a majority of cases, the precipitates produced by these reagents will indicate the acid present, and it only remains to confirm it by the reactions given for that acid. In some cases, it may be of advantage to have the acids classed in groups, and for this reason the acids that are likely to be met are arranged in three groups, according to the plan before indicated. If the student has done his work thoroughly up to this point, he will experience no difficulty in determining the rarer acids, if called upon to do so, and as they would merely serve to complicate matters, if introduced here, they will be disregarded.

TABLE 3.

ACIDS PRECIPITATED BY SILVER NITRATE.

Acid.	Color of Precipitate.	Solubility.
Hydrochloric	White.	Insoluble in HNO_3.
Hydrobromic	Yellowish white.	Insoluble in HNO_3.
Hydriodic	Yellow.	Insoluble in HNO_3.
Thiosulphuric	White, turns black on standing.	Soluble in HNO_3.
Sulphurous	White, turns gray on boiling.	Soluble in HNO_3.
Hydrosulphuric	Black.	Insoluble in cold dilute HNO_3.
Phosphoric	Yellow.	Soluble in HNO_3.
Carbonic	White.	Soluble in HNO_3, with effervescence.
Chromic	Red.	Soluble in HNO_3.
Silicic	Yellow.	Soluble in HNO_3.
Nitrous	White (from concentrate solutions).	Soluble in HNO_3.
Hypochlorous	White.	Insoluble in HNO_3.
Boric	White (from concentrate solutions).	Soluble in HNO_3.
Hydrocyanic	White.	Insoluble in HNO_3.
Hydrosulphocyanic	White.	Insoluble in cold dilute HNO_3.
Hydroferrocyanic	White.	Insoluble in HNO_3.
Hydroferricyanic	Yellow.	Insoluble in HNO_3.
Oxalic	White.	Soluble in HNO_3.
Tartaric	White.	Soluble in HNO_3. Boiling precipitates gray metallic silver.
Formic		Precipitates gray metallic silver upon standing for some time in the cold or more readily upon heating.

Benzoic and *salicylic* acids are classed in the second group, but must be recognized by their special reactions.

TABLE 4.

ACIDS PRECIPITATED BY LEAD ACETATE.

Acid.	Color of Precipitate.	Solubility.
Hydrochloric....	White.	Soluble in hot water.
Hydrobromic....	White.	Soluble in HNO_3.
Hydriodic.......	Yellow.	Soluble in hot water.
Sulphuric.......	White.	Insoluble in HNO_3.
Thiosulphuric...	White.	Soluble in HNO_3.
Sulphurous......	White.	Soluble in HNO_3.
Hydrosulphuric..	Black.	Soluble in warm HNO_3.
Phosphoric......	White.	Soluble in HNO_3.
Carbonic........	White.	Soluble in HNO_3, with effervescence.
Chromic........	Yellow.	Soluble in concentrate HNO_3.
Boric...........	White.	Soluble in HNO_3.
Hydrofluoric....	White.	Soluble in HNO_3.
Hypochlorous...	White, turning to brown on standing.	
Silicic..........	White.	Soluble in HNO_3.
Hydrocyanic....	White.	Soluble in HNO_3.
Hydroferrocyanic	White.	Insoluble in HNO_3
Oxalic..........	White.	Soluble in HNO_3.
Tartaric........	White.	Soluble in HNO_3.
Citric...........	White.	
Malic...........	White.	
Salicylic........	White.	
Benzoic.........	White, from alkali benzoates.	

The four rare organic acids given in this table are precipitated as given if the conditions are right, but other reactions must be depended upon to identify them.

The acids of the first group are those precipitated by barium chloride. They are: *sulphuric, thiosulphuric, sulphurous, chromic, phosphoric, carbonic, boric, hydrofluoric, silicic, oxalic, and tartaric acids.*

The second group is composed of the acids that are not precipitated by barium chloride, but form precipitates with silver nitrate. This group contains: ***hydrochloric, hydrobromic, hydriodic, hydrosulphuric, hydrocyanic, hydroferrocyanic, hydroferricyanic, and hydrosulphocyanic acids.***

The third group contains those acids that are not precipitated by either of these reagents. They are: ***nitric, chloric, and acetic acids.***

Nitrous acid is also sometimes classed in this group, but generally in the second group. By looking at its reactions it will be seen that its classification is doubtful.

It must be remembered that we cannot use the filtrate from the first group of acids to test for the second group, for in that case the barium chloride, added as the first reagent, will precipitate the silver of the silver nitrate as silver chloride. Separate solutions must always be used, and in applying tests for the acids of the third group, some of the original solution must be used.

SPECIAL TESTS FOR ACIDS.

146. Having now located the acid within very narrow limits, special tests are next applied. One or two of the most characteristic tests for each of the common acids are given in the following list. After determining the acid by one of these tests, it should always be confirmed by the other reactions given for that acid.

1. **Hydrochloric acid,** when treated with silver nitrate, gives a white precipitate of silver chloride $AgCl$, which is easily dissolved by ammonia, and is reprecipitated by nitric acid. Sodium thiosulphate also dissolves the precipitate.

2. **Hydrobromic acid,** treated with silver nitrate, gives yellowish-white silver bromide $AgBr$, which is dissolved with some difficulty in ammonia, but readily by sodium thiosulphate.

The most characteristic test for hydrobromic acid in the case of a solid bromide is made by heating it in a test tube with concentrate nitric acid, when reddish-brown vapors of bromine are given off, and condense in the upper part of the tube, forming red globules. This test may be applied to all solid bromides except the bromide of silver, and can also be applied to concentrate solutions.

3. **Hydriodic acid** gives yellowish silver iodide AgI when treated with silver nitrate. The precipitate is almost insoluble in dilute ammonia, but is dissolved somewhat by concentrate ammonia, and is readily soluble in sodium thiosulphate.

A chloride may be recognized in the presence of bromides and iodides by precipitating all of them with an excess of silver nitrate, and dissolving the silver chloride with a mixture of equal parts of dilute ammonia and water. After filtering, the silver chloride may be reprecipitated from the alkaline filtrate by nitric acid. To distinguish bromides and iodides when all three acids are present, place a small quantity of the solution in a test tube, add a few drops of colorless carbon bisulphide, which will form a globule, and then add a saturated solution of chlorine water, drop by drop, and shake the tube frequently. The chlorine water will first set the iodine free, and this will give the globule a violet tint; a few more drops of chlorine water destroys this color, and sets bromine free, imparting a yellow color to the globule, which is in turn destroyed by an excess of the chlorine water.

4. **Sulphuric acid**, when treated with barium chloride, gives white barium sulphate $BaSO_4$, which is insoluble in all acids. Lead acetate precipitates white lead sulphate $PbSO_4$, which may be dissolved by adding tartaric acid, and then rendering alkaline with strong ammonia.

5. **Thiosulphuric acid**, when treated with silver nitrate, gives, at first, a white precipitate that turns brown, and finally

becomes black, owing to its reduction to silver sulphide Ag_2S. All thiosulphates are decomposed by hydrochloric acid, yielding sulphur dioxide and free sulphur.

6. **Sulphurous acid,** when treated with silver nitrate, precipitates white silver sulphite Ag_2SO_3, which is decomposed into gray metallic silver and sulphuric acid by boiling. All sulphites are decomposed by hydrochloric acid, yielding sulphur dioxide, which is recognized by its odor.

7. **Hydrosulphuric Acid.**—Nearly all sulphides are decomposed when heated with concentrate sulphuric acid, and yield hydrogen sulphide, which is recognized by its odor. All precipitates of acids containing sulphur, when fused on the charcoal with sodium carbonate, form sodium sulphide. If this fusion is placed on a piece of silver, ground up, and a drop or two of water added, it leaves a black stain on the silver, due to the formation of silver sulphide.

8. **Phosphoric Acid.**—If a drop or two of phosphoric acid, or a solution of a phosphate in nitric acid, are added to about 2 cubic centimeters of hot ammonium-molybdate solution in a test tube, a yellow precipitate of ammonium phosphomolybdate is formed at once. This precipitate is soluble in ammonia, and is reprecipitated by nitric acid. Arsenious and arsenic acids, if present, must be removed by hydrogen sulphide before applying this test, as they also give yellow precipitates, though not so readily as phosphoric acid.

9. **Carbonic Acid.**—Hydrochloric acid decomposes all carbonates with effervescence, which is due to escaping carbon dioxide. Effervescence indicates a carbonate, and this conclusion may be confirmed by testing the escaping gas with a drop of barium hydrate on a glass rod. Carbon dioxide renders the barium hydrate turbid.

10. **Chromic Acid.**—Yellow normal chromates are changed to red bichromates by rendering them acid with

nitric or hydrochloric acid. The red bichromates are changed to yellow normal chromates by ammonia. All chromates, in solutions containing free acid, are reduced to green chromium compounds when heated with alcohol or sulphurous acid. The borax-bead test is also a good one; but, when it is applied, it must be remembered that all compounds containing chromium, either in the base or in the acid, give the color to the bead. Compounds containing chromium in the base are green, while the chromates are yellow or red.

11. **Nitric Acid.**—To the solution to be tested for nitric acid, add an equal volume of concentrate sulphuric acid, and cool by allowing water to run over the outside of the test tube. When cool, hold the tube in an inclined position and carefully add 1 or 2 cubic centimeters of ferrous sulphate, in such a manner that the liquids do not mix, but the sulphate forms a separate layer above the solution to be tested. If nitric acid is present, a dark ring will be formed where the two solutions meet. This test is sometimes varied by dropping a crystal of ferrous sulphate into the solution instead of adding the ferrous-sulphate solution. In this case, the crystal is surrounded by a dark color that gradually spreads to the rest of the solution.

12. **Boric Acid.**—Mix the substance to be tested for boric acid with concentrate sulphuric acid, in a porcelain dish; add alcohol, stir, and heat the contents of the dish, and then ignite the alcohol. The characteristic green flame is conclusive proof of boric acid. The free acid gives the flame without being mixed with sulphuric acid, but nearly all the borates are non-volatile.

13. **Silicic Acid.**—Solutions to be tested for silicic acid may be rendered distinctly acid with hydrochloric acid, and evaporated to dryness in a porcelain dish. The residue is treated with hydrochloric acid to dissolve any metals present, and silicic oxide will remain as an undissolved residue. This may be separated from the solution, removed to a platinum

crucible, and dissolved in hydrofluoric acid. Upon heating, the silicon tetrafluoride formed is volatilized, leaving the crucible empty.

For solid silicates, the *silica skeleton* in the microcosmic bead, described in Art. **132,** 6, gives an easy means of recognizing the acid. This reaction may be performed, using any precipitate obtained from silicic acid.

14. **Arsenious and Arsenic Acids.**—These acids have been treated among the metals where they are always found in the course of analysis. Arsenious acid is precipitated at once from acid solutions by hydrogen sulphide, as yellow arsenious sulphide. Arsenic acid is first reduced to arsenious by the hydrogen sulphide, and is then precipitated. Heat promotes the reduction and precipitation. They may be further identified by their reactions with silver nitrate. Neutral solutions of arsenites produce a yellow, and arsenates a red, precipitate.

15. **Hydrocyanic Acid.**—To test a solution of hydrocyanic acid, mix about 2 cubic centimeters of it in a test tube with from half a dozen to a dozen drops of ferrous sulphate and 2 or 3 drops of ferric chloride, add sodium hydrate till the mixture is distinctly alkaline, and heat nearly to boiling. Then add hydrochloric acid in sufficient quantity to produce a distinctly acid reaction. If much hydrocyanic acid is present, a deep-blue precipitate will be formed, and if but little of the acid is present, it will give a blue coloration. This test may be applied to insoluble cyanides by first fusing them with sodium carbonate. During the fusing, the hydrocyanic acid unites with sodium, forming soluble sodium cyanide. This is dissolved in about 2 cubic centimeters of water and the solution treated as described above. The reaction with silver nitrate, which is similar to that of hydrochloric acid, is quick and simple, and may serve to identify this acid in many cases.

16. **Hydrosulphocyanic acid** imparts an intense red coloration to a dilute solution of ferric chloride. The color

is not injured by hydrochloric acid, but is destroyed by mercuric chloride.

17. **Hydroferrocyanic Acid.**—In acid solutions of hydroferrocyanic acid or ferrocyanides, ferric chloride produces a dark-blue precipitate of ferric ferrocyanide $Fe_4'''Fe_3''(CN)_{18}$ known as Prussian blue.

18. **Hydroferricyanic acid,** and solutions of ferricyanides, when treated with ferrous sulphate, yield a blue precipitate of ferrous ferricyanide $Fe_3'''Fe_2''(CN)_{12}$, which is insoluble in dilute acids. This precipitate is known as Turnbull's blue.

147. Writing Reports.—In reporting analyses, the student should adopt a neat and uniform system of writing his results. In commercial work, the exact form adopted is a matter of personal preference, but in sending analyses of the substances, sent with the Question Paper, to the Schools, the following forms should always be followed. In order to illustrate the method of using these blanks, analyses are reported on the forms.

1. *Where one metal is to be determined in a solution.*

QUESTION NO.__

Reagent.	Precipitate.	Conclusion.
1. H_2S.	Black.	*Ag*, *Pb*, *Hg*(*ous*), *Hg*(*ic*), or *Cu*. Possibly *Bi* or *Sn*.
2. $NaOH$.	Yellow.	*Hg*(*ic*).

REMARKS.—Mercury in the mercuric condition was indicated as above, and confirmed by the usual reactions. Therefore, No.__ is a solution of a mercuric compound.

[Signature, etc.] ....

2. *Determination of several metals in a solution.*

QUESTION No.__

Group.	Precipitate.	Conclusion.
I.	White.	Possible metals—$Ag, Pb, Hg(ous)$. Metals found—Ag.
II.	Black.	Possible metals—All of the group. Metals found—Bi, Cu.
III.	None.	Possible metals—None. Metals found—None.
IV.	Light colored.	Possible metals—Mn, Zn. Metals found—Zn.
V.	None.	Possible metals—None. Metals found—None.
VI.	None.	Possible metals—None. Metals found—None.
VII.	Odor of NH_3. No flame test.	Ammonium is present, but sodium and potassium are not.

REMARKS.—The above metals were found and confirmed in the usual manner. The solution contains a mixture of compounds of silver, bismuth, copper, zinc, and ammonium.

[Signature, etc.] ____________________

3. *When metal and acid are both determined.*

QUESTION No.__

METAL.

Reagent.	Precipitate.	Conclusion.
1. H_2S.	Black.	$Ag, Pb, Hg(ous), Hg(ic), Cu$. Possibly Bi or Sn.
2. $NaOH$.	Blue, black on boiling.	Cu.

REMARKS.—Copper was determined as shown above, and confirmed by the other reactions for copper.

ACID.

Reagent.	Precipitate.	Conclusion.
1. $BaCl_2$.	White, insoluble in acids.	Acid of the first group. Probably H_2SO_4.
2. $Pb(C_2H_3O_2)_2$.	White, soluble in tartaric acid and ammonia.	H_2SO_4.

REMARKS.—Sulphuric acid was found as above, and confirmed by the *coin test* and other reactions.

CONCLUSION.—The compound is copper sulphate $CuSO_4$.

[Signature, etc.] ....

QUALITATIVE ANALYSIS.

(PART 2.)

XAMINATION OF DRY SUBSTANCES.

PRELIMINARY REMARKS.

As we now have before us all the information neces- for the analysis of any common inorganic substance in tion, the next step will be the analysis of dry substances. dry reactions are short and simple, and in many cases l positive results very quickly. In case of some complex tances that do not give positive results by this method, s are obtained that render their analysis by the wet 1od much easier, after putting them into solution by one 1e methods given later.

1 this, as in every part of the work, the student should merely follow directions, but should make use of all of knowledge of chemistry, and study carefully the cause of phenomenon that he observes. Physical properties, as the color and form of many substances, give valu- indications in regard to their composition, and in some s the substances are so strongly indicated in this way it is only necessary to confirm them by a few reactions. as a rule, a systematic course of treatment should be ued. The most common operations are six in number, are generally applied in the following order:

1. *Heat the substance in a closed tube.*

2. *Heat the substance on the charcoal before the blowpipe.*

3. *Heat the substance in the non-luminous flame on a loop of platinum wire.*

4. *Heat the substance in the borax or microcosmic bead.*

5. *Fuse the substance on the platinum foil with sodium carbonate and potassium nitrate.*

6. *Heat the substance with concentrate sulphuric acid in a test tube.*

One of these tests will show that the substance is one of a number of compounds. The next will reduce the possible number, or perhaps indicate the compound, and each succeeding test reduces the number, until we arrive at a result. It seldom happens that all six tests are applied to any one substance, for, when a previous test has shown that a certain operation will not yield any information, it is, of course, omitted.

The above scheme is based upon the supposition that the substance is *not* a metal or an alloy. If its appearance indicates that it *is* one of these, it is treated by a method to be given later.

EXAMINATION IN THE CLOSED TUBE.

2. If the substance is in the form of a powder, or in small crystals, it is ready for analysis; if in lumps or large crystals, it must first be pulverized. A small quantity of it is introduced into the tube and shaken down into the closed end. The quantity should not exceed half an inch in the bottom of the tube. This is heated gently at first, and finally at the highest temperature of the Bunsen flame. The points to be observed are:

1. *If water is driven off and condenses in the upper part of the tube.*

2. *If any gas escapes.*

3. *If there is any change of color.*

4. *If sublimation takes place.*

5. *If the substance fuses.*
6. *If the substance carbonizes.*

3. Water is Expelled.—If water is driven off, it shows that the substance belongs to one of the following classes:

1. *Substances containing water of crystallization.* Many of these fuse at first, and solidify as the water is driven off. Some of them, especially alums, borates, and phosphates, swell up as the water is being driven off.

2. *Hydrates, or compounds containing chemically combined water.*

3. *Salts that contain mechanically enclosed water*, in which case they usually decrepitate.*

4. *Deliquescent substances.*

5. *Ammonium salts that are decomposed with the formation of water.* Ammonium nitrate is the most common of these, and in its case nitrous oxide N_2O is formed at the same time, and will ignite a spark on the end of a splinter held at the mouth of the tube. The reaction of the water that condenses in the tube should always be tested with litmus paper. An alkaline reaction indicates the presence of ammonium compounds, and an acid reaction indicates a salt of a volatile acid.

Certain minerals possess the property of decrepitating without giving off water, when heated.

4. A Gas or Vapor is Evolved.—If a gas or vapor is given off, the color, odor, and reaction with litmus paper should be observed. It should also be tested to see if it is combustible, and if it will rekindle a spark on the end of a splinter.

The most common gases given off at this point are the following:

1. *Oxygen* is recognized by its power of reigniting a glowing spark on the end of a splinter of wood, when it is

* By saying that a substance *decrepitates* is meant that when heated it breaks up violently into small pieces, which tend, if not confined, to fly some distance. This is usually accompanied with a crackling sound.

held at the mouth of the tube. It indicates nitrates, chlorates, metallic peroxides, or oxides of the noble metals.

2. *Sulphur dioxide* is recognized by its odor and its acid reaction. It is produced when sulphites and some sulphates are decomposed by heat, and also when some sulphates and sulphides are mixed and ignited.

3. *Nitrogen peroxide* is known by its brownish-red color and peculiar odor, and indicates nitrates or nitrites—especially those of the heavy metals.

4. *Carbon dioxide* indicates carbonates or oxalates of metals that are reducible. The gas is odorless, colorless, and non-combustible. It is recognized by its property of rendering turbid a drop of barium hydrate, and by extinguishing a spark held in the mouth of the tube.

5. *Carbon monoxide* indicates oxalates or formates. It is recognized by the blue flame with which it burns when ignited. In the case of formates of easily reducible metals, and of a number of oxalates, carbon dioxide is also given off, and this makes it difficult to ignite the carbon monoxide. Formates often char to a considerable extent in the closed tube, while this is very rare with oxalates. When mixed with a little manganese dioxide and a few drops of water on a watch glass, and a little concentrate sulphuric acid is added, oxalates give off carbon dioxide, while formates do not. This gives us a convenient method of distinguishing between these two acids.

6. *Chlorine*, *bromine*, and *iodine* indicate certain chlorides, hypochlorites, bromides, and iodides, which are broken up by heat. They may be recognized by their odor and color. Chlorine is yellowish green; bromine, brownish red; and iodine, violet. If given off in any considerable quantity, iodine forms a black sublimate in the upper part of the tube.

7. *Hydrogen sulphide* indicates sulphides that contain water, or thiosulphates. It is readily recognized by its odor, and, if evolved in sufficient quantity, when ignited, burns with a pale-blue flame having a red mantle, forming sulphur dioxide and water.

8. *Cyanogen* and *hydrocyanic acid* indicate cyanides that

are decomposed by heat. They are known by their peculiar odor, similar to that of bitter almonds. Cyanogen, when free from other gases, will burn with a crimson flame, if ignited.

9. *Ammonia*, which is recognized by its odor and alkaline reaction, indicates ammonium salts. Nitrogenous organic matter or cyanides containing water may also give it off; but in this case the substance usually chars, and the ammonia is generally mixed with other vapors having disagreeable odors.

10. *Nitrous oxide* indicates ammonium nitrate, or an ammonium salt mixed with a nitrate. It is recognized by its power of supporting combustion, which is almost as great as that of oxygen. If ammonium nitrate alone is present, its decomposition products will be completely volatilized, leaving the tube clean.

5. A Change of Color.—If the substance changes color, the colors before heating, while hot, and after cooling, should be observed.

1. If the substance changes from white to yellow when hot, and becomes white again upon cooling, it indicates zinc oxide ZnO, or a compound of zinc, like the carbonate, which is readily reduced to oxide when heated.

2. A change from white or light yellow to yellowish brown when hot, turning to dirty light yellow upon cooling, indicates stannic oxide SnO_2.

3. If the substance changes from light yellow to yellowish red or brownish red when hot, returning to yellow on cooling, and fuses at a high temperature, it indicates lead oxide PbO.

4. A change from red to brown when hot, turning red again on cooling, indicates red lead oxide Pb_3O_4. Intense heat expels part of the oxygen from this, forming the yellow oxide PbO.

5. A change from white or light yellow to orange yellow or reddish brown when hot, turning to pale yellow on cooling, indicates bismuth oxide Bi_2O_3.

6. A change from a light yellowish color to dark brown,

remaining dark brown after cooling, indicates manganous oxide MnO, or a compound, as the carbonate, which is readily reduced to oxide by heat.

7. A change from yellow to dark brown, turning light reddish brown on cooling, indicates cadmium oxide CdO, or a compound, such as the carbonate, that is reduced to the oxide by heat.

8. A change from light blue or light green to black, with the evolution of water, when hot, remaining black when cold, indicates a hydrate or carbonate of copper, changing to oxide, or a similar change in the corresponding compounds of nickel.

9. A change from brownish red to black when hot, turning to brownish red again upon cooling, indicates ferric oxide Fe_2O_3.

10. A change from grayish white to black when hot indicates ferrous carbonate $FeCO_3$.

11. A change from yellow to dark orange, the substance fusing at an intense heat, indicates potassium or sodium chromate.

12. A change from light red to dark red, and then almost black upon raising the temperature, turning light red again upon cooling, indicates mercuric oxide HgO. In this case, intense ignition decomposes the compound, with the evolution of oxygen and the formation of a sublimate of metallic mercury in the upper part of the tube.

6. A Sublimate Is Formed.—If a sublimate forms, it shows the presence of a volatile body. By observing the color and other properties of the sublimate, many substances may be recognized.

The most common substances giving a white sublimate are as follows:

1. *Ammonium salts*, which may be verified by the characteristic odor of ammonia given off when the substance is heated with a few drops of sodium hydrate.

2. *Mercurous chloride*, which sublimes without fusing, is yellow when hot, but turns to white on cooling.

3. *Mercuric chloride* first fuses, then fills the tube with dense white fumes that condense in the upper part of the tube in the form of a white crystalline sublimate.

4. *Lead chloride* fuses to a yellow liquid and then volatilizes, forming a white sublimate that is volatilized with difficulty.

5. *Arsenious oxide* volatilizes without fusing, and forms a white crystalline sublimate. If a little powdered charcoal is introduced into the tube, and heat applied, it reduces the oxide, and a dark arsenic mirror is produced.

6. *Antimonious oxide* fuses to a yellow liquid, and sublimes at a bright-red heat in the form of brilliant, white, needle-shaped crystals.

7. *Oxalic acid* gives off thick fumes that are irritating, and provoke coughing when inhaled. They condense in the upper part of the tube, forming a white crystalline sublimate.

8. *Salicylic acid*, when gently heated, volatilizes without decomposition, forming a white crystalline sublimate. It may be recognized by the odor of phenol, which is given off when it is quickly and intensely heated.

9. *Benzoic acid* is volatilized by heat, without decomposition, giving off irritating fumes that induce coughing when inhaled. The fumes condense in the upper portion of the tube, forming a white crystalline sublimate.

The most common substances giving a yellow sublimate are as follows:

1. *Sulphur* is dark red when hot, but becomes yellow again on cooling. When heated to rather a high temperature in the presence of air, it burns to sulphur dioxide. It may indicate free sulphur, or may result from the decomposition of a metallic persulphide, such as FeS_2, Sb_2S_5, etc.

2. *Arsenious sulphide* gives a sublimate that is red while hot, but usually turns to yellow upon cooling.

3. *Mercuric iodide* forms a yellow crystalline sublimate, that turns red when rubbed with a glass rod, probably owing to a change in crystalline form.

The common substances giving a dark-colored sublimate are as follows:

1. *Iodine* gives off violet vapors that condense on the sides of the tube, forming a black sublimate that often appears to have a violet tinge at the edges, where the sublimate is very thin.

2. *Mercury* and *amalgams* form globules in the tube. In many cases these globules are very minute, and give the sublimate the appearance of a gray mirror.

3. *Mercuric sulphide* yields a black sublimate that becomes red when rubbed with a glass rod.

4. *Arsenic* and arsenides give a brownish-black shining mirror, but no globules are formed. The vapors that are given off have the characteristic garlic odor by which arsenic may always be recognized.

7. The Substance May Fuse Without Apparent Decomposition.—This indicates some compound of one of the alkalies, or one of a few compounds of the alkaline earths, such as a nitrate, a chloride, or a bromide. If, upon intense ignition, a gas is given off, and small fragments of charcoal dropped in the tube are energetically attacked when they come in contact with the fused mass, a nitrate or chlorate is indicated. The gas evolved in this case is oxygen.

8. The Substance Carbonizes.—If the substance carbonizes, or chars, it shows the presence of organic matter. This is always accompanied by the evolution of gases, and by water that is usually either acid or alkaline to litmus paper. If the substance is entirely composed of organic matter, it will be completely consumed when ignited on the platinum foil. Much may be learned of the composition of a substance by noting the odor of the evolved gas. An odor like that of burning hair indicates an organic compound containing nitrogen. The odor of acetone indicates an acetate. An odor like that of burnt sugar indicates a tartrate. If the residue in the tube effervesces when treated with dilute acid, and the original substance did not effervesce when similarly treated, it shows that the substance was composed of an

organic acid combined with an alkali, or alkaline-earth metal, and that this has been reduced to a carbonate by the heat. If this carbonate is soluble in water and gives an alkaline reaction with litmus paper, we may assume that the organic acid was combined with an alkali metal. If the carbonate is insoluble in water, it indicates that the acid was united to an alkaline-earth metal.

Compounds containing an organic acid combined with a metal that is easily reduced, often leave the uncombined metal in the tube. In this case the oxygen of the oxide is removed by the carbon that is thrown out during the reaction, leaving the metal, and much or all of the carbon unites with the oxygen, leaving little or none in the tube.

9. The Substance Remains Unchanged.—If the substance is not altered by the heat, it shows the absence of organic matter, salts containing water of crystallization or constitution, compounds that are easily fused, those that change color when heated, and volatile compounds, except carbon dioxide, which may be given off without being observed in any way except by applying a test at the mouth of the tube.

EXAMINATION ON THE CHARCOAL.

10. Place a little of the substance to be tested in a small cavity that has been made for the purpose in a piece of fine-grained, soft-wood charcoal, and by means of the blowpipe, direct the flame upon it, heating gently at first, and afterwards to the highest temperature obtainable. One of the objects of this treatment is to see if the substance is fusible, and it should be noted whether the substance fuses easily, with difficulty, or is infusible. After trying this, the substance should be exposed to the inner, or reducing, flame, to see if it can be reduced to the metallic state by the combined action of the inner blowpipe flame and the carbon of the charcoal. Most of the reactions observed in the closed tube will be repeated on the charcoal, and a number of others

added. The phenomena here observed may lead to the direct detection of the composition of the substance, or reduce the number of possible compounds within very narrow limits.

11. The Substance Decrepitates.—This indicates one of a number of crystalline substances, some of which contain water of crystallization, or substances containing water mechanically enclosed. Of the crystalline substances that decrepitate, sodium chloride (common salt) is probably the most common.

12. The Substance Deflagrates.—If the substance deflagrates (i. e., burns violently), a nitrate or chlorate is indicated, and more particularly nitrates and chlorates of the alkalies. Deflagration is caused by the carbon of the charcoal uniting with the oxygen set free when chlorates or nitrates are decomposed by the heat. The residue left on the charcoal should be tested. If the substance was a nitrate, a carbonate will be left on the charcoal, and may be recognized by treating part of it with dilute hydrochloric acid, when it will effervesce. If the substance was a chlorate, a residue of chloride will be left on the charcoal, and may be identified by one of the tests for hydrochloric acid.

13. The Substance Fuses.—If the substance fuses and penetrates the charcoal, or forms a bead in the cavity, without giving an incrustation, gas, or odor, and without changing color, a salt of an alkali, or one of a few compounds of the alkaline earths, is indicated. To distinguish between these, first place a small quantity of the substance in a test tube, add a little strong solution of sodium hydrate, and heat. If an ammonium compound is present, ammonia will be evolved, and is recognized by its odor. Next, bring a little of the substance into the flame on the loop of a platinum wire, and observe the color imparted to the flame, both with and without the blue glass. After holding it in the flame for a short time, dip it into hydrochloric acid, and again bring it into the flame. The colors imparted to the flame by the metals

are: sodium, yellow; potassium, violet; barium, green; strontium, crimson; and calcium, brick red.

14. The Substance Volatilizes.—If the substance volatilizes, it indicates one of the compounds of mercury, arsenic, antimony, or ammonium, or organic substances.

The student should be very careful not to inhale much of the vapors given off by these compounds, as they are very injurious. It is a good plan to make it a rule not to breathe any of the vapors produced by substances that give sublimates in the closed tube; or, if we do so in order to detect the odor in the case of arsenic, to be very careful not to inhale much.

15. A Metallic Globule is Formed.—1. If, upon the sustained application of a strong flame for some time, a metallic globule is obtained, and no incrustation is formed, it indicates that the substance was a compound of gold, copper, silver, or tin. If the globule is yellow, gold is indicated; if red, it indicates copper; and silver or tin is indicated if a white globule is formed. In the case of tin and silver, incrustations are formed, but they are often so slight as to be overlooked, and so are mentioned here. The compounds of platinum, iron, cobalt, and nickel are also reduced; but, if pure, these metals cannot be fused into globules by the blowpipe flame.

2. A white, soft, and malleable metallic globule, with a yellow volatile incrustation that becomes lighter colored upon cooling, indicates a compound of lead. In this case the flame is usually colored blue when the incrustation is volatilized, especially if the reducing flame is used.

3. If the metallic globule is white, hard, and brittle, and fuses easily, and the incrustation is dark orange yellow when hot, but changes to lighter yellow upon cooling, and is volatile, but does not color the flame, a compound of bismuth is indicated.

4. A metallic globule that is easily fused and slowly volatilized, together with a reddish-brown incrustation that

volatilizes without coloring the flame, indicates a compound of cadmium.

5. If the metallic globule is white, hard, and brittle, and the incrustation is white and volatile, a compound of antimony is indicated.

6. If a white, rather hard, but malleable globule is formed and a very slight, dark-red incrustation is deposited, silver compounds are indicated. If small quantities of lead and antimony are present, the incrustation will be crimson.

7. A bright, readily fusible metallic globule that is malleable, together with an incrustation that closely surrounds the globule and is faint yellow while hot, but becomes white upon cooling, indicates a compound of tin. The incrustation is often very slight, and the metallic globule is only obtained by persistent heating in the reducing flame, or by special treatment to be described later.

16. An Incrustation is Formed Without a Metallic Globule.—It will be noted that some of the metals that were mentioned as giving metallic globules are also mentioned here. The reason for this is that some of the compounds of these metals may yield a metallic globule, while it is impossible to obtain it from others by ordinary means; hence, they must be treated under both heads.

1. A white incrustation that forms on the charcoal at some distance from the test, and volatilizes very easily when heated, giving a garlic odor, indicates a compound of arsenic.

2. A reddish-brown incrustation that volatilizes easily before the flame without imparting a color to it, indicates a compound of cadmium.

3. A white incrustation that forms rather near the test, and is so volatile that it may be driven from place to place on the charcoal, indicates a compound of antimony.

4. A dark reddish-yellow incrustation that becomes lemon yellow on cooling, and may be volatilized without coloring the flame, indicates a compound of bismuth.

In the case of antimony and bismuth, metallic globules are usually—though not always—formed.

5. An incrustation that is deposited rather near the test, is yellow while hot, but turns to white upon cooling, and is volatilized with difficulty, indicates a compound of zinc.

6. An incrustation that surrounds the test closely, is yellowish white while hot, and white when cold, and is not volatile, indicates a compound of tin.

7. A reddish-brown incrustation that imparts a deep-green color to the flame indicates a compound of thallium.

17. An Infusible Metal.—If the substance does not give an incrustation, but is reduced to the metallic state without forming a globule, owing to the infusibility of the metal, a compound of platinum, iron, chromium, cobalt, nickel, or manganese is indicated. By heating a little of the metal in the borax or microcosmic bead, chromium, cobalt, and manganese may be identified, and the others more or less clearly indicated.

18. A White, Luminous, Infusible Mass.—If a white mass that is infusible, and is incandescent when highly heated, is formed on the charcoal, either at once or after water is expelled, it indicates a compound of tin, aluminum, zinc, barium, strontium, calcium, magnesium, silicic oxide, or, possibly, a silicate. A drop or two of cobalt-nitrate solution should be added, and the mass again heated in the oxidizing blowpipe flame to the highest temperature obtainable. By this means the test is generally given a characteristic color.

1. *Blue* indicates aluminum oxide, or a compound that has been reduced to the oxide, a phosphate of an alkaline-earth metal, or possibly silicic oxide, or a silicate.

2. *Green* indicates an oxide of zinc or tin, or one of their compounds that has been reduced to the oxide. Stannic oxide is colored rather a bluish green.

3. *Rose color* indicates magnesium oxide that may have been formed by the reduction of some other compound on the charcoal. Magnesium phosphate gives a violet-colored residue.

4. *Gray* indicates an oxide of barium, strontium, calcium,

one of their compounds that has been reduced to the oxide, or, possibly, silica, or a silicate. If a small piece of the test, placed on a piece of red litmus paper, and moistened with a drop of water, colors the paper blue, it indicates barium, strontium, or calcium, as the oxides of these metals give an alkaline reaction. The same test may be applied in the case of magnesium, as its oxide is also alkaline. To distinguish between barium, strontium, and calcium, moisten a small piece of the test on a platinum wire with hydrochloric acid, dry it carefully near the flame, moisten again with hydrochloric acid, and bring it into the outer flame, when the metal will impart its characteristic color to the flame. The colors imparted by strontium and calcium are very similar under certain circumstances, and care should be taken to distinguish between them.

Silicic oxide (silica) and silicates may be recognized by heating a small portion of the substance in a microcosmic bead, when the silica skeleton will be formed if silicon is present.

19. A Colored Mass.—If a colored residue that is only slightly luminous when heated is left on the charcoal, it indicates a compound of copper, iron, chromium, cobalt, nickel, or manganese, or some compound of sulphur. The metals named may be distinguished from one another with a fair degree of accuracy by means of the borax or microcosmic bead, and by fusing on the platinum foil with sodium carbonate and potassium nitrate, as previously described.

If a compound of sulphur is present, it may be recognized by mixing some of the substance with sodium carbonate and fusing it on the charcoal, when sodium sulphide is formed, which, when ground up on a piece of silver and moistened with a drop or two of water, will deposit a black stain of silver sulphide. In performing this operation, it is sometimes necessary to heat the mixture, at the highest temperature obtainable, with the reducing blowpipe flame for some time, in order to reduce the compound and form sodium sulphide.

20. In the case of oxides and other easily reducible compounds, such as nitrates, the substance will be reduced to the metallic state when heated alone on the charcoal, in the reducing blowpipe flame, if it is a compound of a reducible metal; but, in case of compounds that are difficult to reduce, such as sulphates, sulphides, chlorides, phosphates, etc., the reduction is greatly facilitated by adding sodium carbonate. By this means double decomposition is induced, and the oxide is formed, and from this we may be able to obtain the metal. In many cases reduction is greatly aided by mixing the substance with about twice its volume of potassium cyanide, and heating this mixture in the reducing blowpipe flame on the charcoal, or by heating the substance with a mixture of sodium carbonate and potassium cyanide. If a metallic globule is obtained by any of these methods, it should be examined as to its color, hardness, brittleness, and malleability. In case the globule is sufficiently large, it may be removed from the charcoal with the forceps, placed on a smooth piece of steel, and examined with the aid of a hammer. If the globules are small, they should be scraped out, together with the adhering charcoal, into a small mortar, a little water added, and the charcoal loosened from the metal by gently rubbing with a pestle. The charcoal is then carefully washed out by means of water, and the metal left in the mortar, where it may be examined by means of the pestle, or it may be removed to the smooth steel and a hammer used, as in the case of large globules. If the metal is yellow, gold is indicated; copper is indicated if the metal is red; silver is white; tin, grayish white; cadmium, bluish white; lead, whitish gray; bismuth, reddish gray; and antimony, gray. Lead and tin are soft and malleable; gold and cadmium are harder than lead and tin, but not very hard, and are malleable; copper and silver are rather hard, but are malleable, and bismuth and antimony are hard and brittle. After examining the globule in this way, it is best to dissolve it in acid, and apply the wet reactions. It is impossible to reduce the alkalies and alkaline-earth metals to the metallic state by any treatment on the charcoal.

Many of the reactions observed in the closed tube will also appear when the substance is heated on the charcoal, and indicate the same things here that they do in the closed tube. Thus, ammonia, which is always recognized by its odor, indicates a compound of ammonium, etc.

EXAMINATION IN THE FLAME.

21. As we have already seen, a number of substances impart characteristic colors to the flame when heated in it; and, as the operation is simple and quickly performed, it gives us a good method of determining these substances. In performing this operation, be sure that the platinum wire is perfectly clean, by burning it off till it does not color the flame, after it has been suspended in hydrochloric acid; and, while hot, bring the loop in contact with some small particles of the substance to be tested. They will adhere to the hot wire, and may be brought into the outer flame, when they will impart the characteristic color to the flame, if the substance is one that colors the flame. If the substance does not color the flame, it should be dipped in hydrochloric acid, and brought into the flame again. If it does not color the flame now, dip it into sulphuric acid, and again bring it into the outer flame, as this is necessary in order to set free phosphoric or boric acid. When compounds of sodium are present, they give such an intense color as to often obscure the colors of the other substances, so that it is very often necessary to view the flame through a blue glass. The following colors when obtained are quite characteristic:

1. *Yellow* indicates a compound of sodium. It is often so intense that it is impossible to see the colors imparted to the flame by other substances that may be present; so, when a flame is colored an intense yellow, it should be viewed through a blue glass, when the yellow rays will be absorbed and other shades will appear.

2. *Violet* indicates a compound of potassium.

3. *Bright red* or *crimson* indicates a compound of

strontium or lithium. There is a slight difference in these flames, which serves to indicate more or less clearly to the experienced chemist which metal is present; but this reaction alone cannot be depended on to identify either of these metals with certainty; they may, however, be distinguished easily by other means, as lithium forms no compounds insoluble in water, while strontium forms many.

4. *Brick red* indicates a compound of calcium. Under certain conditions, the color imparted to the flame by calcium compounds is almost as bright a red as that given by strontium or lithium, but this is rather unusual.

5. *Blue* indicates a compound of lead, antimony, arsenic, or copper chloride $CuCl_2$. All compounds of copper, except the chloride, impart a green color to the flame.

6. *Green* indicates a compound of barium, copper, thallium, molybdenum, manganese chloride, boric acid, or phosphoric acid. Molybdenum gives a rather yellowish-green color to the flame; volatile compounds of boric acid impart a bright green, which often lasts but a moment, and phosphoric acid a rather pale green. Borates and phosphates must be treated with sulphuric acid before trying the flame reaction. Phosphates may sometimes fail to color the flame, but borates always impart a green color, especially if treated with sulphuric acid and alcohol and ignited in a porcelain dish, as described in treating the reactions of boric acid.

EXAMINATION IN THE BEAD.

22. Compounds of many of the metals, when heated in the borax or microcosmic bead, impart a color to the bead by which these metals are indicated. The colors imparted by three of these metals—chromium, cobalt, and manganese—are so distinctive as to be conclusive proof of the presence of these metals, and the others may be recognized with tolerable certainty by this test, after the operator has become familiar with them. In making this test, first be sure the wire is perfectly clean; then, while it is hot, dip the loop

into powdered borax, or microcosmic salt, and heat the portion that adheres to the hot wire until it fuses into a clear, transparent bead; and while this is hot bring it in contact with a few small particles of the substance to be tested, which will adhere to the soft, hot bead. Only a very small quantity of the substance should be taken for this purpose. Now heat the bead containing the substance, in the oxidizing flame, until it is thoroughly fused, and observe the color of the bead when hot, while cooling, and after it is cold. Then hold the bead in the reducing flame for some time, and note any change that may take place either while the bead is hot or after it cools. The following are the most important metals that give colored beads, with the colors which they impart.

A blue bead in both the oxidizing and the reducing flame, that appears more clearly colored upon cooling, indicates cobalt.

An amethyst-red bead showing the color much better after cooling, and becoming colorless, but not quite clear, when heated in the reducing flame, indicates manganese.

A green bead, in both the oxidizing and the reducing flame, that becomes particularly clear and distinct upon cooling, indicates chromium.

A bead that in the oxidizing flame is bluish green when hot, and blue when cold, and becomes red in the reducing flame after considerable of the substance has been added, indicates copper.

A bead that in the oxidizing flame is brownish red, and changes to yellow or becomes colorless upon cooling, and in the reducing flame is red while hot, yellow while cooling, and yellowish green when cold, indicates iron.

A bead that in the oxidizing flame is red when hot, but becomes yellowish brown, yellow, or even colorless upon cooling, and in the reducing flame is reddish brown when hot, and becomes gray and opaque when cool, indicates nickel.

A bead that in the oxidizing flame is yellow when hot and becomes lighter colored—sometimes almost colorless—on cooling, and in the reducing flame is yellow or almost

colorless when hot, and gray and opaque when cold, indicates bismuth.

An infusible skeleton floating in the fused bead indicates silicic oxide or a silicate. For the silicates, a microcosmic bead must be used.

A bead that, when heated in the oxidizing flame, is light yellow or opal while hot, and turbid when cold, and becomes whitish gray in the reducing flame, indicates silver.

In the case of sulphides and arsenides, the substance should be heated on the charcoal with the blowpipe until the sulphur or arsenic is driven off, as these may interfere with the bead reaction to a certain extent, and a little of the residue is used in the bead.

The most important of the bead reactions may be given in the form of a table for convenience:

TABLE 1.

O. F.	*Metal.*	*R. F.*
Blue	*Co*	Blue
Amethyst	*Mn*	Colorless
Green	*Cr*	Green
Hot.—Bluish green *Cold.*—Blue	*Cu*	Red when cold
Hot.—Brownish red *Cold.*—Yellow or colorless	*Fe*	*Hot.*—Red *Cold.*—Yellowish green
Hot.—Red *Cold.*—Yellow	*Ni*	*Hot.*—Red *Cold.*—Gray and opaque
Hot.—Yellow *Cold.*—Light yellow	*Bi*	*Hot.*—Light yellow *Cold.*—Gray and opaque

EXAMINATION ON THE PLATINUM FOIL.

23. Examination on the foil is only resorted to in cases where chromium or manganese has been indicated by some of the preceding tests, when it is used to confirm these metals. Care must be taken not to fuse compounds of such metals as lead or mercury on the foil, or they will alloy with the

platinum and destroy the foil. To perform this operation, mix a little of the substance with about its own volume of potassium nitrate, and three times its volume of sodium carbonate, on the foil, and heat till it is thoroughly fused. If manganese is present, it is oxidized to manganate and gives the fusion a deep-green color, which is a very characteristic reaction for manganese. When the fusion is dissolved in boiling water, the manganese is precipitated as a brown oxide. If a chromium compound is present, it will be oxidized to chromate of sodium or potassium, and will give the fusion more or less of a yellow tint. In this case the fusion should be dissolved in equal parts of acetic acid and water, the solution boiled until all carbon dioxide is expelled, and lead acetate added. If chromium is present, yellow lead chromate will be precipitated. The precipitate is soluble in sodium hydrate, and is reprecipitated from this solution by nitric acid. The fusion is dissolved in acetic acid and water, rather than water alone, in order to break up the carbonate and expel the carbon dioxide, which, if present, would precipitate the lead as carbonate, and obscure the reaction with the chromate.

EXAMINATION WITH SULPHURIC ACID.

24. Treatment with sulphuric acid is for the purpose of detecting the acid present, and much may be learned of the composition of a substance by this means. To make this test, place a small amount of the substance in a test tube, add about 2 or 3 cubic centimeters of concentrate sulphuric acid; heat gently at first, then gradually raise the heat to the boiling point. During this heating, some of the following gases may be liberated, which will lead to the identification of the acid.

1. *A colored gas is given off.* It may be:

Chlorine, which is recognized by its yellowish-green color and peculiar, penetrating odor, indicates a hypochlorite, a mixture of a chloride and a nitrate, or a chloride and a

peroxide. These latter may suffer double decomposition, during which chlorine is liberated. A greenish-yellow explosive mixture of chlorine and chlorine tetroxide indicates a chlorate. In case a chlorate has been indicated by a previous reaction, only a very little of the sample should be taken, as a larger quantity is likely to cause a violent explosion, which is dangerous, as it may spatter the hot concentrate acid.

Yellowish vapors of *bromine*, which are generally mixed with some hydrobromic acid, may be recognized by their color and odor, and indicate a bromide. In case a bromide is thus indicated, a small quantity of the substance should be heated with concentrate nitric acid, which decomposes all bromides, except the bromide of silver, giving off reddish vapors that condense in red globules in the upper part of the tube.

Dark-red vapors of *chromium oxychloride* CrO_2Cl_2 indicate a mixture of a chloride and a chromate.

Reddish-brown fumes of *nitrogen tetroxide* N_2O_4, which are recognized by their color and odor, and which indicate a nitrite. Nitrites are decomposed in the same way when heated with dilute sulphuric acid.

Violet vapors of *iodine*, which condense, forming a black solid in the upper part of the tube, and show the presence of an iodide.

2. *A colorless gas with an odor may be given off.* The most common are:

Hydrochloric, or, possibly, *hydrobromic*, acid. These are recognized by their odors, and by the white fumes that are produced when they come in contact with a drop of ammonia held at the mouth of the tube on a glass rod. They indicate salts of these acids. Hydrobromic acid is always more or less decomposed by the heat of the reaction, and brownish vapors of bromine may be seen.

Hydrofluoric acid, known by its penetrating odor and white fumes, but especially by its power of etching glass, shows the presence of a fluoride.

Sulphur dioxide, known by its penetrating odor, like that

of burning sulphur matches, indicates a sulphite or thiosulphate.

Hydrogen sulphide, recognized by its disagreeable odor, and its property of blackening a piece of filter paper that has been moistened with a solution of lead or silver, indicates a sulphide.

Nitric acid, which is indicated by its odor, and by the brown fumes that are given off when a small crystal of ferrous sulphate is dropped into the tube, indicates a nitrate. In this case the contents of the tube should be cooled, and ferrous-sulphate solution cautiously added, when the characteristic brown ring will be formed where the two solutions meet.

Hydrocyanic acid, which is recognized by its peculiar odor, similar to that of bitter almonds, indicates a cyanide.

Acetic acid, which is recognized by its odor, indicates an acetate. In this case a little of the substance should be heated with concentrate sulphuric acid and alcohol, when acetic ether, having an agreeable odor somewhat like that of ripe apples, is evolved.

A gas having an odor like that of burnt sugar, accompanied by a charring of the substance, indicates *tartaric acid* or one of its compounds.

3. *A colorless, odorless gas may be evolved.* It may be:

Oxygen, which is recognized by its power of igniting a spark on the end of a splinter when held in the mouth of the tube, indicates a peroxide, a chromate, or a permanganate.

Carbon dioxide, which is evolved with effervescence, and renders turbid a drop of barium hydrate or of lime water, held at the mouth of the tube on a glass rod, indicates a carbonate. In this case a little of the substance should be treated in a test tube with hydrochloric acid, as all carbonates are decomposed by hydrochloric acid, with effervescence. A few of the mineral carbonates, however, show but slight effervescence if the acid is dilute.

Carbon monoxide, which is recognized by its burning with a blue flame when ignited at the mouth of the tube, indicates

an organic compound or a ferrocyanide. Oxalic acid or an oxalate gives both carbon monoxide and carbon dioxide, without any charring of the substance. Both of these gases should be identified in the case of an oxalate, by the blue flame, and the reaction with a drop of barium hydrate. Tartrates give off first carbon monoxide, then begin to char and give off a mixture of carbon monoxide and sulphur dioxide, and, finally, the contents of the tube become thick and black, and yield an odor like that of burnt sugar. Formic acid and formates, when heated with concentrate sulphuric acid, are decomposed with the formation of water and carbon monoxide; the latter escapes with effervescence, and burns with a blue flame. If heated with concentrate sulphuric acid and alcohol, ethyl formate is evolved, and is recognized by its peculiar rum-like odor. Citric acid at first yields carbon monoxide, then carbon monoxide mixed with carbon dioxide, which is recognized by its reaction with barium hydrate, and acetone, indicated by its odor. During this time the solution remains clear; but, upon continued heating it assumes a dark color, and sulphur dioxide is given off.

If a white insoluble precipitate is formed during the treatment with sulphuric acid, lead, mercurous, barium, strontium, or calcium compounds are indicated.

25. Metals and Alloys.—If the appearance of the substance indicates that it is a metal or an alloy, it should be examined as to color, hardness, and malleability, and then small portions of it tested with hydrochloric acid, to see if hydrogen is liberated, and with nitric acid, to see if nitrogen dioxide is evolved. If these gases are given off, they prove the substance to be a metal or an alloy. A small portion of the metal should next be heated on the charcoal before the blowpipe. Its behavior here may lead directly to its recognition, or suggest some special test by which it may be identified.

After these preliminary tests, a small portion of the metal is treated in a test tube with a mixture of equal quantities of concentrate nitric acid and water, and heat is applied, if

necessary. By this means all the metals may be classified as follows:

1. Metals that are not acted on by nitric acid, consisting of gold and platinum.

2. Metals that are oxidized by nitric acid, but whose oxides are not soluble to any considerable extent in an excess of the acid, or in water. This group consists of tin and antimony; and, in the presence of these metals, arsenic, and sometimes bismuth, form compounds that are insoluble in nitric acid and water.

3. Metals that, when treated with nitric acid, form nitrates that are soluble in an excess of the acid, or in water. This class includes all the metals, except those mentioned above.

In any case, evaporate most of the excess of acid, and dilute the substance remaining in the tube with about four times its volume of water. If a clear solution is formed, it may be subjected at once to treatment for the group separations. If a metal remains unattacked by the acid, it is filtered off, and the filtrate tested for metals that may have been dissolved; the metal on the filter is then dissolved in aqua regia, and the solution tested for gold and platinum, as directed in the next section, after most of the excess of acid has been driven off by heating carefully, and the solution has been diluted with about four times its volume of water. If a white insoluble mass is formed, it must be filtered off, and the filtrate examined for metals that may have gone into solution. The precipitate will probably be the oxide of tin or antimony, or possibly one or both of these, together with arsenic or bismuth. And, in addition to these, the precipitate may contain undissolved gold or platinum. After washing it two or three times on the filter, it is removed to a porcelain dish and heated with yellow ammonium sulphide. If not all dissolved, filter, wash well on the filter, and treat the filtrate for the separation of tin, antimony, and arsenic, as described in Art. **97**, *Qualitative Analysis*, Part 1. The precipitate may contain gold, platinum, and bismuth. Dissolve it in aqua regia, drive off most of the excess of acid, dilute with water, heat almost to boiling, and lead a current

of hydrogen sulphide through the hot solution until the metals are completely precipitated as sulphides. Filter, remove the precipitate to a porcelain dish, and heat some time with a mixture of equal parts of concentrate nitric acid and water. This will dissolve the bismuth sulphide, and leave the sulphides of gold and platinum unattacked. Filter, and test the filtrate for bismuth. Then dissolve the precipitate in aqua regia, and test for gold and platinum, as directed in Art. **39**, *et seq.* If both gold and platinum are present, they are separated by means of oxalic acid.

SOLUTION OF SOLID SUBSTANCES.

26. As all solid substances, except simple ones that yield positive results in the dry way, should be dissolved, and the solutions subjected to wet analysis, to confirm the results obtained by the dry method, the means of getting them into solution becomes a matter of importance. The method to be pursued will depend on the dry reactions, and it is impossible in a work of this kind to consider every possible case separately, but a general outline may be given from which the student may select the method suited to any particular case. All substances may be divided into three classes, as follows:

1. *Substances soluble in water.*
2. *Substances insoluble in water, but soluble in an acid.*
3. *Substances decomposed by fusing with carbonates.*

As complex substances may contain compounds belonging to each of these classes, a small portion should be heated in a test tube with water, the filtrate tested for compounds that may have gone into solution, and the residue treated with acids. The excess of acid should be driven off after this operation, the substance diluted with water, filtered, the filtrate tested for substances that may have been dissolved, and the residue, if any remains, fused with carbonates of sodium and potassium. By this treatment, all compounds may be dissolved.

As the treatment of metals and alloys has already been described, they will not be considered here.

27. Substances Soluble in Water.—Unless the dry reactions have clearly shown that such treatment would be useless, the first operation should be to boil a little of the substance thoroughly in a test tube with water. All substances that have been fused, must be ground to a fine powder before treatment. If an undissolved residue remains, it should be filtered off, and the clear filtrate examined for compounds that may have been dissolved. The principal substances dissolved by water are:

1. All chlorates, hypochlorites, acetates, and formates.
2. All chlorides, bromides, and iodides, except those of silver, lead, and mercury in the mercurous condition.*
3. All nitrates and nitrites, except a few basic nitrates.
4. All sulphates, with the exception of lead, mercurous, barium, strontium, and calcium sulphates.
5. The alkalies and all their compounds, except metantimonate of sodium and potassium silicofluoride.
6. The chromates of copper, zinc, manganese, ferric iron, and mercury in the mercuric condition.
7. Oxalates of chromium, aluminum, antimony, ferric iron, and tin in the stannic condition.
8. Sulphides of the alkaline earths. The sulphides of calcium and magnesium sometimes dissolve with difficulty.

In addition to these, the cyanides, arsenites, arsenates, acid carbonates, and oxides of the alkaline earths are partially dissolved in water. Calcium sulphate may also be partly dissolved in a large quantity of water.

28. Substances Insoluble in Water.—If the substance is insoluble in water, a portion should be placed in a test tube, concentrate hydrochloric acid added, and the contents of the tube boiled, if necessary. By this means many substances insoluble in water are changed to soluble chlorides,

* Cuprous chloride, bromide, and iodide are insoluble in water; but, as they are not common, and are rapidly oxidized to soluble cupric compounds, they may generally be disregarded.

and water is formed, or the acid, if volatile, is driven off, or, if non-volatile, remains in solution.

If this treatment fails to decompose the substance, a small quantity of it should be heated in a test tube with concentrate nitric acid. This will oxidize some insoluble compounds, forming soluble ones; as, mercurous chloride is oxidized to mercuric, etc.

If the substance is not dissolved by either of these acids separately, it should be boiled with aqua regia. If this fails to dissolve the substance, it must be fused with a carbonate or subjected to some special treatment in order to get it into solution. In each case the excess of acid should be driven off, water added, the substance filtered, and the clear filtrate tested to see if a part of the substance has been dissolved.

In case the substance is dissolved by one of these acids, the excess of acid is driven off, the substance diluted with four or five times its volume of water, and subjected to examination for the metals in the wet way.

29. Substances Fused With Carbonates.—Most substances are decomposed by acids, but a few—including anhydrous silicates, and sulphates of barium, strontium, and, possibly, calcium, although the latter is usually dissolved, partly by water and partly by acids—remain undissolved, and must be put into solution by some other means. The most general method of doing this is to fuse the substance with about six times its weight of a mixture of equal parts of sodium and potassium carbonates. By this means the substances are decomposed, the acid of the substance unites with sodium or potassium, forming soluble alkali salts, and the metal is changed to carbonate. The fusion is made in a platinum vessel, usually the foil, and must be continued until chemical action ceases and the fusion becomes quiet. Substances that would alloy with platinum must not be treated in this manner.

The fusion after cooling is transferred to a test tube or a small beaker, and boiled with water until it is thoroughly disintegrated. The acid, which is combined with an alkali,

will now be in solution, and the carbonate or oxide of the metal will remain undissolved. Filter, and test the filtrate for the acid; then dissolve, in hydrochloric acid, the residue that remains on the filter, and test this solution for the metal.

Pulverized silicates that are insoluble in the acids used may be decomposed by hydrofluoric acid, and this method must be resorted to when the alkalies are to be determined.

Insoluble cyanides, ferrocyanides, and ferricyanides are best dissolved by fusing in a porcelain crucible, with about five times their weight of a mixture of equal parts of sodium and potassium carbonates. The acid unites with the alkalies, forming soluble cyanide, ferrocyanide, or ferricyanide of sodium and potassium, and carbonates or oxides of the metals are formed. After disintegrating the fusion in hot water, and filtering, the acid may be determined in the filtrate. Then the precipitate is dissolved in nitric acid, and the metals determined in this solution.

30. We now have before us all the principal dry reactions, and the general methods of dissolving solid substances. After this has been done, the results obtained in the dry way should always be confirmed by the wet reactions. When an acid is used in dissolving a substance, this solution cannot be used in testing for the acid, for the reactions for the acid used in dissolving the substance will, of course, be obtained.

THE RARE ELEMENTS.

31. The rare elements arrange themselves in the same groups as the common metals, but the distinction between the groups is not so sharp as in the case of the common metals; and, as their treatment at that point would have greatly complicated the work, they were reserved for special treatment in a separate section. The most important reactions, by which these elements may readily be recognized, are given here.

GROUP I.

Thallium Tl *Tungsten W*

32. Thallium.—Thallium is a soft white metal, and is often found in minute quantities associated with sulphides of the other metals, as in copper and iron pyrites. It forms two series of compounds—thallous and thallic—but the latter are very unstable, and are readily reduced to thallous compounds. It is readily dissolved by dilute nitric or sulphuric acid, but is only slightly acted upon by hydrochloric acid. Thallium is not completely embraced in this group, as thallous chloride is slightly, and thallic chloride easily, soluble in water, so that, in dilute solutions of thallous, or ordinary solutions of thallic, compounds, the metal passes on to the fourth group, where it is completely precipitated by ammonium sulphide.

1. Thallic compounds are reduced to thallous compounds with the separation of free sulphur when treated with hydrogen sulphide.

2. *Sodium and ammonium hydrates and carbonates* precipitate brown, gelatinous compounds from thallic solutions, but give no precipitates with ordinary thallous solutions. The carbonates give white precipitates with very strong thallous solutions.

3. *Potassium iodide* precipitates light-yellow thallous iodide TlI from thallous solutions. In thallic solutions the same precipitate is formed, and iodine is set free.

4. *Hydrochloric acid* precipitates white thallous chloride from thallous solutions that are not very dilute, but gives no precipitate with thallic compounds.

5. *Ammonium sulphide* precipitates black thallous sulphide Tl_2S from thallium solutions. Hydrogen sulphide produces the same precipitate from solutions that do not contain inorganic acids, but the presence of inorganic acids prevents this precipitate.

6. All thallium compounds are readily reduced when heated on the charcoal before the blowpipe, and deposit a

dark-violet or black incrustation that is volatile and imparts a green color to the flame.

7. Thallium compounds are best recognized by the deep emerald-green color that they impart to the flame, or by means of the spectroscope. The thallium spectrum consists of one green line. In many cases the flame or the line can only be seen for a short time.

33. Tungsten.—Tungsten is a white, hard, brittle element that is classed with the metals principally on account of its weight and some other physical properties. In nearly all its chemical relations it acts as a non-metal. Its oxygen compounds are all acid. Magnesium tungstate and the alkali tungstates are soluble. All the others are insoluble in water, and many of them in acids. The insoluble tungstates are best decomposed by fusing with carbonates of sodium and potassium, when soluble tungstates of the alkalies are formed.

1. *Hydrochloric acid* precipitates white H_2WO_4, H_2O from cold solutions, and yellow H_2WO_3 from hot solutions. These precipitates are insoluble in an excess of acid, but soluble in ammonia.

2. *Hydrogen sulphide*, when led through a solution of a tungstate that is rendered distinctly acid, reduces the tungstate to a lower oxide, and gives the solution a blue color.

3. *Ammonium sulphide* gives no precipitate in neutral or alkaline solutions of tungstates, but, if an excess of the sulphide is added and then the solution is rendered acid, a light-brown precipitate of tungsten trisulphide WS_3 is formed.

4. *Stannous chloride* gives a yellow precipitate that changes to a fine blue color when hydrochloric acid is added and heat is applied. This is a very characteristic reaction for tungsten.

5. *Metallic zinc* and hydrochloric acid added to a tungstate solution produce a blue color, owing to reduction of the tungsten to a lower oxide W_2O_5.

6. All tungsten compounds, when heated for some time

in the reducing flame, in the microcosmic bead, impart a blue color to the bead. If iron is introduced, the bead assumes a blood-red color; but the blue color is restored by adding a little tin foil, and heating again.

GROUP II.

DIVISION A.

Palladium Pd	*Rhodium Rh*
Osmium Os	*Ruthenium Ru*

34. These rare elements occur associated with platinum almost exclusively. They are all completely precipitated by hydrogen sulphide, and are insoluble in ammonium sulphide and alkaline hydrates, hence they are completely comprehended in this group.

35. Palladium.—Palladium always occurs associated with platinum, and is nearly always present, in small quantities, in platinum ores. It is obtained from the residue that is left when platinum is extracted from its ores. It is lighter than platinum, is white, malleable, and ductile, and only fuses at very high temperatures. It is more easily oxidized, and is less dense than platinum. It has both divalent and tetravalent relations, but the compounds in which it acts as a divalent element are much more common and stable. It is not dissolved by hydrochloric acid, and is only slightly acted on by nitric acid, but is readily dissolved to $PdCl_2$ by aqua regia.

1. *Ammonium hydrate* precipitates, from palladium solutions, flesh-colored palladammonium chloride $Pd(NH_3)_2Cl_2$, which dissolves in an excess of ammonia, especially when heated, forming a colorless solution from which it is reprecipitated in yellow crystals by hydrochloric acid.

2. *Sodium hydrate* precipitates a brown basic salt that is slightly soluble in an excess of the reagent.

3. *Hydrogen sulphide* precipitates black palladious sulphide PdS from slightly acid solutions of palladium. The precipitate is insoluble in ammonium sulphide, but dissolves slowly in hot concentrate hydrochloric acid, and readily in aqua regia.

4. *Ammonium sulphide* gives the same reaction as hydrogen sulphide.

5. *Mercuric cyanide* precipitates yellowish-white palladious cyanide $Pd(CN)_2$ from neutral or slightly acid solutions. The precipitate is slightly soluble in hydrochloric acid, and is readily dissolved by ammonia. This reaction is very characteristic, and it is important as the means of separating palladium from the residuary solution in the platinum process. The cyanide is decomposed by heat, leaving the palladium in the spongy form. This is known as ***palladium sponge.***

6. *Stannous chloride* in the presence of free hydrochloric acid gives the solution at first a red color, which quickly changes to brown, and finally becomes greenish. Upon the addition of considerable water, this changes to reddish brown.

7. *Potassium iodide* precipitates black palladious iodide PdI_2, which is soluble in considerable excess of the precipitant, forming a dark-brown solution. This reaction is very characteristic.

8. *Potassium sulphocyanide* does not precipitate palladium, even after the addition of sulphurous acid. This gives us the best means of separating palladium from copper.

36. Osmium.—Osmium is a very rare element, but it occasionally occurs in platinum ores alloyed with iridium. It is usually obtained as a black or gray powder, with metallic luster, and is the most infusible metal known. Metallic osmium, osmious oxide OsO, osmium trioxide Os_2O_3, and osmic oxide OsO_2 are all readily oxidized to osmium tetroxide OsO_4 when heated in the air. This is a very volatile compound, with an exceedingly irritating and offensive odor, similar to that of chlorine and bromine, and gives us the best means of recognizing osmium.

If a little osmium is held in the outer non-luminous flame on a platinum wire, it makes the flame exceedingly luminous. By this means the presence of osmium is indicated in alloys of osmium and iridium. If only minute quantities of osmium are present, the flame is only rendered highly luminous for a very short time; but, by holding the alloy in the reducing flame for a time, and then returning it to the outer flame, this may be repeated.

Fuming nitric acid and aqua regia dissolve osmium, forming the tetroxide. The application of heat hastens the solution, and volatilizes the tetroxide, which is recognized by its odor.

Osmium tetroxide, when heated with water, first fuses, and then slowly dissolves to a colorless liquid, with an unpleasant, irritating odor.

1. *Hydrogen sulphide* gives this solution a dark-brown color; and when an acid is added, a dark-brown precipitate of osmium sulphide OsS_4 is formed. This is insoluble in ammonium sulphide and alkali hydrates.

2. *Sulphurous acid* produces at first a yellow color, which, upon the addition of more of the reagent, changes to reddish brown, then green, and finally blue.

3. *Zinc*, added to an acid solution, precipitates metallic osmium.

4. All compounds of osmium, when ignited in hydrogen, yield the metal, but, when ignited on the charcoal in the oxidizing flame, yield volatile osmium tetroxide, which is recognized by its odor.

37. Rhodium.—Rhodium occurs in very small quantities in platinum ores. In the compact form it is a silver-white, malleable metal, which fuses with great difficulty, and is insoluble in all acids. When precipitated from solution it is a gray powder, dissolving somewhat in concentrate nitric acid. A solution of rhodium is best obtained by fusing the metal or one of its salts in acid potassium sulphate, and dissolving the fusion in water or hydrochloric acid. The solution in water is yellow, and the hydrochloric-acid solution is red.

1. *Sodium hydrate* precipitates yellow rhodium hydrate $Rh(OH)_3, H_2O$, which is changed to dark brown or black $Rh(OH)_3$ by boiling.

2. *Hydrogen sulphide*, when led through a hot rhodium solution for some time, precipitates brown rhodium sulphohydrate $Rh_2(SH)_6$ which is insoluble in alkali sulphides and in single acids, but is dissolved by aqua regia. When this precipitate is boiled with considerable water, it is decomposed into hydrogen sulphide H_2S and rhodium sulphide Rh_2S_3.

3. *Zinc*, added to an acid solution, precipitates black metallic rhodium.

38. Ruthenium.—Ruthenium, like the other rare metals of this group, is chiefly found associated with platinum. In the compact form it is a grayish-white brittle metal that is exceedingly difficult to fuse. When precipitated, it is a grayish-black powder. It is scarcely acted upon by aqua regia, and is unaffected when fused with acid potassium sulphate. A solution of ruthenium is best obtained by fusing for some time with a large excess of potassium nitrate. After cooling, the fused mass dissolves in water to an orange-colored solution of potassium ruthenate K_2RuO_4. A few drops of nitric acid precipitate dark-brown ruthenium trioxide Ru_2O_3, which is dissolved in hot concentrate hydrochloric acid. This solution is used for the following reactions:

1. *Hydrogen sulphide*, when led through this solution for some time, produces a light-colored precipitate of unknown composition. Upon continued treatment, the precipitate becomes darker, and when nearly black, if the precipitate is filtered off, a deep sky-blue filtrate is obtained.

2. *Ammonium sulphide* precipitates brownish-black ruthenium trisulphide Ru_2S_3, which is almost insoluble in an excess of the reagent.

3. *Potassium iodide*, added to a cold solution, slowly precipitates black ruthenic iodide RuI_4. If added to a hot solution, the black precipitate is formed at once.

4. *Zinc*, added to the acid solution of the chloride, at first imparts a blue color to the solution, owing to the reduction to ruthenious chloride, and finally precipitates black metallic ruthenium.

DIVISION B.

Gold Au	*Platinum Pt*	*Iridium Ir*
Molybdenum Mo	*Selenium Se*	*Tellurium Te*

39. Gold.—Gold is usually found in the metallic state. In this condition it is recognized by its yellow color, malleability, and insolubility. It is insoluble in any single acid, but is readily dissolved by aqua regia, forming $AuCl_3$. It acts both as a monovalent and as a trivalent element, but in most of its compounds it is trivalent.

1. *Hydrogen sulphide* precipitates brownish-black gold sulphide Au_2S_3 from a cold solution of the trichloride. The precipitate dissolves slowly in colorless ammonium sulphide, but more readily in yellow ammonium sulphide, and the solution is promoted by heating. It is not dissolved by any single acid, but dissolves readily in aqua regia.

2. *Ammonium sulphide* precipitates brownish-black gold sulphide Au_2S_3, which dissolves in an excess of the reagent, especially when heated. It dissolves more readily in yellow ammonium sulphide, and is still more easily dissolved by yellow sodium sulphide.

3. *Ferrous sulphate* reduces the gold chloride, and precipitates metallic gold, in a very finely divided reddish-brown powder. When held up and looked at towards the light, the liquid in which the gold is suspended appears bluish by the transmitted light.

4. *Stannous chloride*, which contains some stannic chloride, produces a purple precipitate, known as "purple of Cassius." This precipitate is decomposed, with the separation of metallic gold, by hydrochloric acid. The mixture of stannous and stannic chlorides is obtained by adding a few drops of chlorine water to stannous chloride.

5. *Sulphurous acid* reduces the chloride, and finely divided

metallic gold separates, and is suspended in the solution. Upon boiling, this settles to the bottom of the tube as a black powder.

6. *Oxalic acid*, when heated with a solution of gold chloride that does not contain too much free acid, reduces the gold to the metallic state, and gives off carbon dioxide, sometimes with effervescence. After decanting the liquid, the gold may be fused into a metallic globule. This is best done in a porcelain crucible. The reaction with oxalic acid affords the best means of separating gold from other metals, especially platinum.

40. Platinum.—Platinum in the compact form is a rather hard, very malleable and ductile, steel-gray metal that fuses only at very high temperatures, and is insoluble in any single acid, but dissolves in aqua regia. Platinum sponge is dull gray, and precipitated platinum is a black powder, known as *platinum black*. When platinum is dissolved in aqua regia, if an excess of hydrochloric acid is present, platinum chloride $PtCl_4$ is formed. After driving off the excess of acid by gentle heat, and diluting with water, a solution is obtained that is suitable for the following reactions:

1. *Hydrogen sulphide*, when led into a cold platinum solution, at first colors the solution brown, and then slowly precipitates brownish-black platinum sulphide PtS_2. If the solution is heated, the precipitate forms at once. Ammonium and sodium sulphides, especially when heated, dissolve this precipitate, but the solution is slow, and it is difficult to dissolve it completely. Hot concentrate nitric acid slowly dissolves the precipitate that is formed in the cold, but scarcely acts on the sulphide precipitated from hot solutions. It dissolves in aqua regia.

2. *Ammonium sulphide* precipitates brownish-black platinum sulphide PtS_2, which is slightly soluble in an excess of the reagent, and more easily dissolved by yellow ammonium or sodium sulphide. Heat aids the solution.

3. *Ferrous sulphate* does not produce a precipitate in

solutions of platinum chloride, except upon long-continued boiling, in which case platinum finally separates.

4. *Stannous chloride* does not precipitate platinum from its solutions, but imparts a dark-red or reddish-brown color to the solution.

5. *Potassium iodide*, when added in excess to an ordinary platinum solution, produces a dark-red coloration. If the solution is very dilute, a rose-red color is obtained.

6. *Oxalic acid* does not precipitate platinum from its solutions. This gives us the best means of separating gold and platinum. If, to a solution of these metals that contains a slight excess of hydrochloric acid, oxalic acid is added and the solution boiled, all the gold will be precipitated and the platinum will remain in the solution. After the gold is filtered off, the platinum may be precipitated as sulphide, or we may add ferrous sulphate to the solution, render it alkaline with sodium hydrate, then add hydrochloric acid, and heat, when the platinum will be precipitated as platinum black.

41. Iridium.—Iridium is found associated with other metals in platinum ores, especially with osmium as an alloy of osmium and iridium known as *osmiridium*. In the compact condition it is a heavy, steel-gray, brittle metal that fuses only at very high temperatures. In compact form, or when reduced from its compounds by hydrogen at a red heat, all acids, even aqua regia, fail to dissolve it—a fact that serves to distinguish it from gold and platinum. When precipitated from a solution, or when alloyed with a large amount of platinum, aqua regia dissolves it, forming the tetrachloride $IrCl_4$. Acid potassium sulphate oxidizes, but does not dissolve it, thus serving to distinguish it from rhodium. When fused with potassium nitrate, it is oxidized, and may be partially dissolved in water. If the fusion is heated with aqua regia, the iridium is completely dissolved, forming a dark-red solution of iridic chloride $IrCl_4$.

1. *Hydrogen sulphide* at first reduces the iridic chloride to iridious chloride Ir_2Cl_6, and sulphur is thrown out. The

solution assumes an olive-green color. But, upon continued treatment, brown iridious sulphide Ir_2S_3 is precipitated.

2. *Ammonium sulphide* precipitates brown iridious sulphide Ir_2S_3, which is easily dissolved in an excess of the reagent.

3. *Zinc*, added to a solution of iridic chloride containing free hydrochloric acid, reduces it and deposits metallic iridium as a black powder.

4. *Ferrous sulphate*, *sulphurous acid*, and *oxalic acid* do not precipitate iridium.

42. Molybdenum.—Molybdenum is found in small quantities as molybdenum sulphide and as lead molybdate. All its compounds when heated in the air are changed to molybdic oxide MoO_3, which is soluble in ammonia. If hydrochloric acid is added to this solution, it precipitates the white oxide, which dissolves in more of the acid. This solution gives the following reactions:

1. *Hydrogen sulphide* at first gives the solution a blue color, and then precipitates dark-brown molybdenum sulphide MoS_3, while the supernatant liquid becomes green. The precipitation is not complete in the cold, but, by heating the solution and treating for some time with hydrogen-sulphide gas, the molybdenum is all precipitated. The precipitate dissolves in alkali sulphides, and is reprecipitated from this solution by hydrochloric acid.

2. *Zinc*, when added to the hydrochloric-acid solution, soon develops a blue, green, or brown color, depending on the degree of concentration of the solution.

3. *Stannous chloride* imparts a blue, green, or brown color to the solution, depending on the amount of the reagent added, and the concentration of the solution.

4. *Ferrous sulphate*, containing free sulphuric acid, gives the solution a blue color that is permanent.

5. *Sodium phosphate*, added to a molybdate solution containing a little free nitric acid, produces at once, or upon gently heating, a yellow precipitate of phosphomolybdate, which is insoluble in nitric acid, but is soluble in an excess

of the reagent. Ammonia also readily dissolves the precipitate, and from this solution it is reprecipitated by nitric acid.

6. All molybdenum compounds, when heated in the oxidizing blowpipe flame on the charcoal, deposit an incrustation of molybdic oxide, which is yellow when hot, and white or yellowish white when cold.

43. Selenium.—Selenium is classed with the nonmetals. It occurs principally as lead selenide $PbSe$. In many respects it resembles sulphur. Selenium and most of its compounds are soluble in nitric acid or aqua regia, but the selenides of lead and silver dissolve with difficulty. All selenium compounds, when fused with a mixture of sodium carbonate and potassium nitrate, form alkaline selenates that are soluble in water, and the solution remains clear when acidified with hydrochloric acid. If the solution is boiled with hydrochloric acid, chlorine is given off, and selenic acid is reduced to selenious acid. This solution gives the following reactions:

1. *Hydrogen sulphide*, conducted into a cold solution, produces a yellow precipitate that is probably a mixture of finely divided selenium and free sulphur. If led into a hot solution, a reddish-yellow precipitate of selenium sulphide SeS_2 is obtained. This is soluble in ammonium sulphide.

2. *Stannous chloride* precipitates finely divided selenium, which remains suspended in the liquid for some time, giving the solution a reddish color. It finally settles to the bottom in the form of a reddish-gray powder.

3. *Sulphurous acid* gives the same reaction as stannous chloride.

4. *Barium chloride*, added to a selenious acid or a selenite solution in which the excess of hydrochloric acid has been neutralized, precipitates white barium selenite $BaSeO_3$, which is soluble in nitric and in hydrochloric acid.

5. Selenium is most readily recognized by heating any of its compounds on the charcoal in the reducing blowpipe flame, when a red incrustation is formed, and a putrid odor

similar to that of decaying horseradish is observed. The incrustation is volatilized by the blowpipe flame, and gives off the characteristic putrid odor.

44. Tellurium.—Tellurium has many of the physical properties of the metals, and on this account is sometimes classed with them. But, chemically, it acts as a non-metal, and is generally classed as such. It resembles sulphur and selenium, and belongs to this group of elements. It occurs in small quantities in nature, combined with gold, silver, or lead. It is white and brittle, fuses easily, and may be sublimed in the closed tube. Tellurium is insoluble in hydrochloric acid, but dissolves readily in nitric acid, forming tellurous acid H_2TeO_3. If this solution is poured into water, the tellurous acid is precipitated. Tellurous acid H_2TeO_3 and its anhydride TeO_2 are readily dissolved by hydrochloric acid, and this solution gives the following reactions:

1. *Hydrogen sulphide* precipitates dark-brown tellurous sulphide TeS_2, which dissolves readily in ammonium sulphide.

2. *Stannous chloride*, *sulphurous acid*, or *zinc*, added to a rather strongly acid solution, precipitates the tellurium as a black powder. This action is aided by warming the solution.

3. *Sodium hydrate* or *carbonate* precipitates white tellurium hydrate, which is soluble in an excess of the reagent.

4. Solid tellurium compounds, when heated on the charcoal before the blowpipe, deposit a white incrustation of tellurous oxide TeO_2, which has a yellowish color when hot.

5. Tellurium compounds, when fused on the charcoal with sodium carbonate, form soluble sodium telluride, which, when placed on a piece of silver and moistened, gives a black stain, similar to that produced by sulphur compounds.

6. When held in the flame on a loop of platinum wire, tellurium imparts a bluish-green color to the flame.

7. If a little finely pulverized telluride ore is covered with water in a porcelain dish, a little mercury added, and then some sodium amalgam, the water is given a violet color by sodium telluride going into solution.

GROUPS III AND IV.

45. As the distinction between the third and the fourth group is not sharp, it is much better to disregard it entirely and treat the two groups as one. This is rendered more practicable in this case by the fact that it is seldom necessary to make a general separation of the rare elements. In a great majority of cases, it is only necessary to determine the presence of one or a very few of them, which may be done by applying the reactions given for the separate elements. This division includes:

Titanium Ti	*Vanadium V*	*Uranium U*
Beryllium Be	*Indium In*	*Gallium Ga*
Zirconium Zr	*Cerium Ce*	*Yttrium Y*
Didymium Di	*Thorium Th*	

46. Titanium.—Titanium occurs in quite large quantities in nature, in clay and some iron ores, and in a number of minerals. It is not used in commerce, and, consequently, is not frequently met in the laboratory. It is most frequently met in the form of titanic oxide TiO_2. Titanic oxide is not dissolved by any acid except hydrofluoric acid, and somewhat in concentrate sulphuric acid. When the solution in hydrofluoric acid is evaporated with sulphuric acid, it is neither decomposed nor volatilized. The best means of obtaining a solution of titanium is to fuse the oxide for some time with acid potassium sulphate. The fused mass will dissolve in moderately warm water, but, if the solution is boiled, metatitanic acid is precipitated. The solution as obtained above may be used for the following reactions.

1. *Ammonium hydrate* precipitates white, flocculent titanic acid H_2TiO_3, which is insoluble in excess, but is dissolved by hydrochloric or dilute sulphuric acid.

2. *Sodium hydrate* gives the same reaction as ammonia.

3. *Sodium thiosulphate*, when boiled with rather a dilute solution of titanium, precipitates it completely as metatitanic acid.

4. *Ammonium sulphide* precipitates white titanic acid H_2TiO_3, which is insoluble in excess of the reagent, but is dissolved by hydrochloric or sulphuric acid.

5. *Zinc*, added to an acid solution of titanium, produces a blue or violet coloration, and, after standing for some time, a blue precipitate separates. Upon standing, this precipitate gradually changes to white. If sodium hydrate is added to the blue solution before the precipitate begins to separate, blue titanium hydrate is precipitated, and on standing gradually changes to white titanic acid.

6. *Potassium ferrocyanide* gives a reddish-yellow precipitate.

7. *Potassium ferricyanide* produces a yellow precipitate.

8. Titanic acid dissolves quite readily in the microcosmic bead, when held in the outer flame near the point of the inner flame, forming a clear colorless bead, that becomes opaque when held at the point of the outer flame. If, instead of holding the bead at the point of the outer flame, it is held for some time in the reducing flame, it is colored yellow while hot, red while cooling, and violet when cold.

47. Vanadium.—Vanadium occurs chiefly combined with lead, and in some iron and copper ores. It is known in several stages of oxidation. VO, V_2O_3, and VO_2 are known, but vanadic oxide V_2O_5, the anhydride of vanadic acid, is the principal oxide. All the lower oxides are oxidized to vanadic oxide, or vanadic acid, by nitric acid or aqua regia, or when fused with potassium nitrate or heated in the air. Vanadic oxide, or acid, dissolves in a large amount of water to a red liquid, or in sulphuric acid to a red or yellow liquid. Moderately dilute sulphuric acid dissolves all of the oxides. In this acid, vanadious oxide VO dissolves to a blue solution, vanadium trioxide V_2O_3 to a green solution, and the dioxide VO_2 to a blue solution. The reddish or yellow solution of vanadic acid in sulphuric acid gives the following reactions:

1. *Ammonium hydrate* produces a brown precipitate that dissolves in an excess of the reagent to a yellowish-brown solution.

2. *Sodium hydrate* gives the same reaction as ammonia.

3. *Hydrogen sulphide* reduces the vanadic acid to vanadium dioxide, and thus colors the solution blue, while free sulphur separates.

4. *Ammonium sulphide* precipitates brown vanadium sulphide V_2S_5, which dissolves with some difficulty in an excess of the reagent to a reddish-brown liquid. From this solution sulphuric acid reprecipitates the brown vanadium sulphide.

5. *Zinc*, added to the acid solution, which is warmed, reduces the vanadic acid, forming at first a blue solution that changes to green, and finally to violet or blue.

6. *Sulphurous acid* reduces the vanadic acid to vanadium dioxide, which imparts a blue color to the solution.

7. *Potassium ferrocyanide* produces a green, flocculent precipitate that is insoluble in acids.

8. Vanadium compounds dissolve in the borax bead in both the oxidizing and the reducing flame, forming clear beads. When a small quantity is heated in the oxidizing flame, a colorless bead is produced, but if much vanadium is present the bead will have a yellow color. If a bead containing a small quantity of vanadium is heated in the reducing flame, a green bead is obtained, while, if more vanadium is present, the bead will be brown when hot, and turn green upon cooling.

48. Uranium.—Uranium occurs in small quantities in nature, principally in pitchblende. There are two oxides, uranous oxide UO_2 and uranic oxide UO_3, and two series of salts. The uranous salts are green, and the uranic compounds are yellow. The latter are by far the more common. Most of the uranic salts are soluble in water, and those that are insoluble in water dissolve in hydrochloric or sulphuric acid.

1. *Ammonium hydrate*, added to uranic solutions, produces a yellow precipitate of ammonium uranate $(NH_4)_2U_2O_7$, which is insoluble in an excess of the reagent.

2. *Sodium hydrate* precipitates yellow sodium uranate $Na_2U_2O_7$, which is insoluble in excess of the reagent.

3. In uranous solutions, ammonium and sodium hydrates give reddish-brown precipitates.

4. *Ammonium sulphide* precipitates, from neutral solutions or acid solutions after neutralizing, brown uranic oxysulphide, which is insoluble in pure colorless ammonium sulphide, but dissolves in yellow ammonium sulphide to a brown solution. The precipitate is dissolved by ammonium carbonate, or by acids. Even acetic acid dissolves it. If the precipitate is boiled in the liquid from which it was precipitated, the oxysulphide is decomposed into uranous sulphide US_2 and free sulphur.

5. *Ammonium carbonate* precipitates yellow ammonium-uranium carbonate $(NH_4)_4UO_2(CO_3)_3$, which readily dissolves in an excess of the reagent. From this solution the uranium is completely precipitated by sodium hydrate, especially when boiled.

6. *Potassium ferrocyanide* produces a reddish-brown precipitate that looks much like copper ferrocyanide, but is distinguished from it by being soluble in ammonia, forming a yellow solution.

7. *Zinc*, added to an acid solution, imparts a green color to the liquid, especially when it is heated. This color is due to the reduction of the uranic to a green uranous compound.

8. Uranium compounds, heated in the borax bead in the reducing flame, impart a green color to the bead that is seen best after the bead cools. Heated in the oxidizing flame, the bead is colored yellow when hot, and assumes a fine yellowish-green color when cold.

49. Beryllium.—Beryllium occurs in nature almost entirely as a silicate. It is associated with aluminum in beryl and emerald. In many respects the compounds of beryllium resemble those of aluminum, but it is divalent, and, therefore, cannot form alums. The soluble beryllium compounds have a sweetish, astringent taste, and give an acid reaction with litmus paper. Most of the silicates are decomposed when heated with concentrate sulphuric acid, and all are readily decomposed when fused with four or five

times their weight of mixed carbonates of sodium and potassium. From solutions of beryllium salts the following reactions are obtained:

1. *Ammonium hydrate* precipitates white, flocculent beryllium hydrate $Be(OH)_2$, which is only slightly soluble in an excess of the reagent. The precipitate looks very much like aluminum hydrate.

2. *Sodium hydrate* precipitates white beryllium hydrate $Be(OH)_2$, which dissolves readily in an excess of the reagent, and the solution remains clear upon boiling, but if considerable water is added, and the boiling continued, beryllium hydrate separates. In this respect it differs from aluminum.

3. *Ammonium carbonate* precipitates white beryllium carbonate $BeCO_3$, which dissolves in a considerable excess of the reagent. This is one of the best methods of distinguishing between beryllium and aluminum. If this solution is diluted with water, and boiled for some time, the beryllium is precipitated as a basic carbonate.

4. *Sodium carbonate* precipitates white beryllium carbonate $BeCO_3$, which is slightly soluble in excess.

5. *Ammonium sulphide* precipitates white beryllium hydrate $Be(OH)_2$.

6. *Oxalic acid* and oxalates do not precipitate beryllium from its solutions, which fact distinguishes it from a number of the other rare metals.

7. Beryllium is separated from aluminum by fusing the mixture with twice its weight of hydrogen-potassium fluoride, and treating the fusion with hydrofluoric acid and water. The beryllium dissolves in this, while the aluminum remains as insoluble potassium-aluminum fluoride.

8. Beryllium compounds, when heated on the charcoal before the blowpipe, yield a mass that is somewhat luminous. When this is moistened with cobalt nitrate, and reignited, it assumes a gray color. In this it differs from aluminum, whose compounds, when similarly treated, are colored blue.

50. Indium.—Indium is found in small quantities, associated with tungsten, and in the blende obtained in certain

localities. It is soft, ductile, fuses easily, and resembles platinum in color. In the air, or in contact with water, it oxidizes, but not quite so rapidly as zinc. The metal dissolves slowly in cold dilute hydrochloric or sulphuric acid, but much more readily if heat is applied. It dissolves readily in cold dilute nitric acid. It is trivalent in all its compounds, and its salts are nearly all colorless. They dissolve in water or acids, forming colorless solutions.

1. *Ammonium hydrate* precipitates white indium hydrate $In(OH)_3$, which is insoluble in excess of the reagent.

2. *Sodium hydrate* precipitates white indium hydrate $In(OH)_3$, which dissolves in an excess of the reagent. From this solution the indium hydrate slowly separates when it is boiled, or when ammonium chloride is added.

3. *Ammonium carbonate* precipitates white indium carbonate $In_2(CO_3)_3$, which is soluble in excess of the reagent, and is reprecipitated from this solution by boiling.

4. *Sodium carbonate* gives the same precipitate as ammonium carbonate, but it is insoluble in excess of the sodium carbonate.

5. *Hydrogen sulphide* precipitates, from neutral solutions or those containing only acetic acid, yellow indium sulphide In_2S_3. The presence of free inorganic acids prevents the precipitation.

6. *Ammonium sulphide* produces a white precipitate of unknown composition. If the yellow indium sulphide is boiled with yellow ammonium sulphide, it becomes white, and partly dissolves. Upon cooling, a white precipitate separates from this solution.

7. *Zinc*, added to an acid solution, precipitates the metal in white shining scales.

8. Indium, when heated on the charcoal, fuses to a bright metallic globule, and deposits an incrustation that is dark yellow when hot, and light yellow when cold, and is only volatilized with difficulty.

9. Indium compounds, held in the colorless flame on a loop of platinum wire, impart a violet-blue color to the flame. Viewed through the spectroscope, this flame gives

two characteristic blue lines. These are the brighest when the chloride is used, but in this case they only last a short time. The lines given by the sulphide are less bright, but are much more persistent.

51. Gallium.—Gallium occurs in very small quantities in some zinc ores. It is a white, hard, slightly malleable metal that dissolves slowly in hot nitric acid, and readily in hydrochloric acid. Its salts are colorless, and the nitrate, chloride, and sulphate readily dissolve in water to colorless solutions.

1. *Ammonium hydrate* precipitates white gallium hydrate $Ga(OH)_3$, which is soluble in excess of the precipitant.
2. *Sodium hydrate* gives the same reaction as ammonium hydrate.
3. *Ammonium carbonate* produces a white precipitate that is soluble in excess of the reagent.
4. *Hydrogen sulphide* does not give a precipitate in solutions containing free mineral acids, but precipitates white gallium sulphide Ga_2S_3 from acetic-acid solutions.
5. *Ammonium sulphide* precipitates white gallium sulphide, which is insoluble in an excess of the reagent.
6. *Potassium ferrocyanide* produces a light, bluish colored precipitate that dissolves more easily in water than in hydrochloric acid.
7. When gallium compounds are held in the Bunsen flame, they give a spectrum consisting of one rather indistinct violet line; but when a spark passes from the positive terminal of an induction coil to the surface of a gallium solution, under which the negative terminal is dipped, the spectrum produced consists of two distinct violet lines. This is the most distinctive reaction for gallium, and the one that led to its discovery

52. Zirconium.—Zirconium occurs as a silicate in a few rare minerals. It is tetravalent, and forms a white infusible oxide ZrO_2, which is luminous when heated. The native minerals are decomposed by fusing, in powdered form, for

some time, with four or five times their weight of sodium carbonate, forming sodium zirconate. The zirconium is dissolved by treating the fused mass with hydrochloric acid, leaving insoluble silicic acid, which may be filtered off. With this solution the following reactions may be obtained:

1. *Ammonium hydrate* precipitates white zirconium hydrate $Zr(OH)_4$, which is insoluble in an excess of the reagent.

2. *Sodium hydrate* gives the same reaction as ammonium hydrate.

3. *Ammonium carbonate* precipitates a white basic carbonate that is soluble in considerable excess of the precipitant. Upon boiling this solution, white, gelatinous zirconium hydrate separates.

4. *Sodium carbonate* gradually precipitates a white basic carbonate that is slightly soluble in an excess of the reagent.

5. *Ammonium sulphide* precipitates white, flocculent zirconium hydrate, which is not dissolved by an excess of the reagent, nor by alkali hydrates.

6. *Oxalic acid* or ammonium oxalate precipitates white, crystalline zirconium oxalate, which is soluble in an excess of the reagent. From this solution, ammonium hydrate reprecipitates the zirconium oxalate.

7. *Sodium thiosulphate*, when boiled with a zirconium solution, precipitates white zirconium thiosulphate, even from dilute solutions.

8. *Hydrogen peroxide* precipitates zirconium in the form of a white, bulky hydrate, probably $Zr(OH)_6$.

9. *Hydrofluoric acid* does not precipitate zirconium from its solutions, which fact serves to distinguish it from yttrium and thorium.

53. Cerium.—Cerium occurs in small quantities in nature, principally as cerous silicate in cerite, and as cerous phosphate in monazite. It exhibits two degrees of valence, forming, with oxygen, cerous oxide Ce_2O_3 and ceric oxide CeO_2. The cerous salts are stable, but ceric salts are readily decomposed, forming cerous compounds. The cerous salts

and their solutions are white or colorless, while ceric compounds and solutions are yellow or red.

Most compounds of cerium may be dissolved by treating the finely powdered compound for some time with concentrate hydrochloric acid. All of its compounds may be decomposed by fusing the pulverized compound with about five times its weight of sodium carbonate. Upon treating the fusion with hydrochloric acid, the cerium dissolves to a colorless solution of cerium chloride $CeCl_3$.

1. *Ammonium hydrate* precipitates a white basic compound that is insoluble in an excess of the reagent.

2. *Sodium hydrate* gives a white precipitate, probably $Ce(OH)_3$.

3. *Ammonium carbonate* precipitates white cerous carbonate $Ce_2(CO_3)_3$, which is only slightly soluble in an excess of the reagent.

4. *Oxalic acid*, added to a solution that does not contain too much free acid, precipitates white cerous oxalate, which is insoluble in an excess of the reagent, but dissolves in a large excess of hydrochloric acid.

5. *Sodium thiosulphate* does not precipitate cerous solutions, even when heated with the concentrate solution, but does form a precipitate with ceric-nitrate solutions.

6. Ceric solutions have a yellow color, but are reduced to cerous compounds by sulphurous acid, and the color is thus destroyed.

7. Cerium oxides are dissolved in the borax bead. In the oxidizing flame the bead is colored yellowish red while hot, and gets lighter colored upon cooling, and sometimes becomes colorless. In the reducing flame the bead is colorless.

54. Yttrium.—Yttrium occurs as a silicate in gadolinite and a few other rare minerals. A solution of yttrium may be obtained by fusing the silicate with sodium and potassium carbonates, and dissolving the fusion in hydrochloric acid. Yttrium forms the oxide Y_2O_3 known as *yttria*. It is slightly soluble in cold nitric, hydrochloric, or sulphuric

acid, and dissolves completely in these acids when heated for some time. Its salts and solutions are colorless. Yttrium solutions give the following reactions:

1. *Ammonium hydrate* precipitates white yttrium hydrate $Y(OH)_3$, which is insoluble in an excess of the reagent, but dissolves in mineral acids. The precipitate also dissolves slowly in ammonium carbonate, and from this solution it is reprecipitated by boiling.

2. *Sodium hydrate* gives the same reaction as ammonium hydrate.

3. *Ammonium carbonate* produces a white precipitate that is somewhat soluble in an excess of the reagent. From this solution it is reprecipitated by boiling.

4. *Sodium carbonate* gives a white precipitate that is slightly soluble in an excess of the precipitant, but dissolves more readily in ammonium carbonate, and is reprecipitated from this solution by boiling.

5. *Ammonium sulphide* precipitates white yttrium hydrate $Y(OH)_3$, which is insoluble in an excess of the reagent, but dissolves in ammonium carbonate or in strong mineral acids.

6. *Oxalic acid* precipitates white yttrium oxalate $Y_2(C_2O_4)_3$, which is insoluble in excess of the reagent, but is partly dissolved by heating with ammonium oxalate. If this solution is diluted and cooled, the oxalate again separates almost completely. The precipitate also dissolves with some difficulty in hydrochloric acid.

7. *Hydrofluoric acid* produces a white gelatinous precipitate that is insoluble in excess of the reagent, and in water. Before it has been heated it dissolves in mineral acids, but after heating it can only be decomposed by concentrate sulphuric acid.

8. When heated on the charcoal before the blowpipe, yttrium oxide is luminous, and emits a white light without fusing.

55. Didymium.—Didymium is found associated with cerium in cerite. It may be separated from cerium by precipitating both the metals as oxalates from a solution obtained

as described under cerium, and heating the precipitate, after it is dry, until the oxalates are broken up, forming oxides; then, by treating the mixed oxides with nitric acid, the didymium is dissolved to a rose-colored solution, while the cerium remains as an insoluble residue.

1. *Ammonium hydrate* precipitates a white basic salt that is insoluble in excess of the reagent, but is dissolved by hydrochloric acid.

2. *Sodium hydrate* gives the same reaction as ammonium hydrate.

3. *Ammonium carbonate* produces a white precipitate that is insoluble in an excess of the reagent, but is soluble in hydrochloric acid.

4. *Sodium carbonate* gives the same reaction as ammonium carbonate.

5. *Oxalic acid* precipitates white didymium oxalate $Di_2(C_2O_4)_3$, which is slightly soluble in cold hydrochloric acid, and dissolves quite readily when the acid is heated.

6. Didymium oxide, when ignited on the charcoal before the blowpipe, appears pure white; but, if a few drops of concentrate nitric acid are added, and it is again ignited at a rather low temperature, it becomes dark brown, owing to the formation of the peroxide DiO_2. If this is again intensely ignited, it changes to the white oxide Di_2O_3.

7. In the oxidizing flame, didymium oxide dissolves in the microcosmic bead, giving it an amethyst color. The color disappears when the bead is held in the reducing flame. It scarcely colors the borax bead, unless large quantities are added.

56. Thorium.—Thorium is a rare metal, and is found in nature, principally as a silicate, in thorite, monazite, etc. The oxide ThO_2, commonly called *thoria*, is important, as it is the chief constituent used in the mantle of the Welsbach light. The native minerals and the artificial compounds are decomposed by treating with rather concentrate sulphuric acid.

1. *Ammonium hydrate* precipitates white thorium hydrate $Th(OH)_4$, which is insoluble in an excess of the reagent. The precipitate is soluble in all inorganic acids while it is

moist, but after heating it is only decomposed by rather concentrate sulphuric acid.

2. *Sodium hydrate* gives the same reaction as ammonium hydrate.

3. *Ammonium carbonate* precipitates a white basic thorium carbonate, which dissolves readily in an excess of the reagent, in a strong solution, but with difficulty if the solution is dilute. Upon heating this solution, the basic carbonate is reprecipitated.

4. *Sodium carbonate* precipitates a white basic carbonate, which is soluble in an excess of the reagent, especially if the solution is strong.

5. *Oxalic acid* precipitates white thorium oxalate $Th(C_2O_4)_2$, which is insoluble in an excess of the reagent, but dissolves in a boiling concentrate solution of ammonium oxalate, and is not reprecipitated when the solution is diluted and cooled. The precipitate also dissolves slightly in dilute inorganic acids, and readily in ammonium acetate containing free acetic acid.

6. *Hydrofluoric acid* precipitates white thorium fluoride ThF_4, which is gelatinous at first, but upon standing changes to a powder. It is insoluble in an excess of the reagent and in water.

7. *Ammonium sulphide* precipitates white thorium hydrate $Th(OH)_4$, which is insoluble in an excess of the reagent, but is dissolved by mineral acids, if treated while still moist.

8. *Sodium thiosulphate*, when boiled with a rather strong solution of thorium, precipitates white thorium thiosulphate, mixed with free sulphur, but the precipitation is not complete, and the precipitate may be colored by the sulphur.

9. *Potassium sulphate*, in concentrate solution, when boiled with a solution of thorium, precipitates the thorium completely as white potassium-thorium sulphate, which is insoluble in an excess of the reagent, and dissolves with difficulty in cold water, but easily in hot water.

10. Thoria is white or gray. When heated on the charcoal before the blowpipe, it is incandescent, and emits an exceedingly brilliant white light.

GROUP VII.

Lithium Li *Cæsium Cs* *Rubidium Rb*

57. Lithium.—Lithium occurs quite widely distributed in nature, but in very small quantities. It is found in many mineral waters, in the ashes of some plants, and in several minerals. In some ways it acts like a fifth, and in some ways like a sixth, group metal, but a majority of its chemical relations place it in this group. The hydrate and the carbonate of lithium dissolve with some difficulty in cold water, but more readily in warm water. Hydrates and carbonates, however, do not precipitate lithium from ordinary solutions. Acid sodium tartrate and platinum chloride do not precipitate lithium from its solutions.

1. *Sodium phosphate*, when boiled with a rather strong lithium solution that has been rendered alkaline with sodium hydrate, precipitates white crystalline lithium phosphate Li_3PO_4, which settles quickly. The precipitate dissolves readily in hydrochloric acid, and when this solution is rendered alkaline by ammonia, no precipitate is formed when cold, but when heated the lithium phosphate again separates. In this, lithium differs from the alkaline earths, and also differs from them in that, when the phosphate is heated on the charcoal before the blowpipe, it fuses and is absorbed into the pores of the charcoal.

2. *Ammonium fluoride*, when added to a rather strong lithium solution, together with an excess of ammonia, gradually precipitates white lithium fluoride LiF. As fluorides of the other alkalies are easily soluble in a mixture of equal parts of ammonium hydrate and water, while it requires 3,500 parts of this mixture to dissolve lithium fluoride, this method may be employed in separating lithium from the other alkalies.

3. All volatile lithium compounds (especially the chloride) impart a bright-red color to the flame, and this is probably the most used of any method in determining lithium. In the presence of large quantities of sodium, the color imparted to the flame by a small amount of lithium is masked by the

yellow sodium flame, and a blue glass must be used to absorb the yellow rays, as in the case of potassium.

4. The best method of detecting small quanties of lithium is by means of the spectroscope. The lithium spectrum consists of a bright-red line and a faint-yellow line.

58. Cæsium and Rubidium.—Cæsium and rubidium are quite widely distributed in nature, but in very minute quantities. They are very closely allied, and resemble potassium, both in compounds and in the color that they impart to the flame.

1. *Platinum chloride* precipitates these metals in the form of double chlorides of the metals and platinum, similar to potassium-platinum chlorides. These precipitates are not nearly so soluble in water as the corresponding double salt of potassium.

2. Cæsium carbonate is soluble in absolute alcohol, while rubidium carbonate is insoluble in that medium, but they cannot be completely separated by this means.

3. Probably the best method of separating these metals is by means of stannic chloride. To do this, add stannic chloride to the hot concentrate solution containing considerable strong hydrochloric acid. The cæsium is precipitated as cæsium-stannic chloride, while the rubidium remains in solution. The precipitate is washed with concentrate hydrochloric acid.

4. Volatile compounds of cæsium and rubidium impart a violet color, similar to that of potassium, to the non-luminous flame; but, when this is viewed through the spectroscope, the spectra of the two metals are very distinct. Cæsium gives two brilliant sky-blue lines and a less distinct red line. Rubidium gives two indigo-blue lines and two bright-red lines. As the flames (and consequently the lines) produced by the chlorides of these metals are more distinct than those produced by the other compounds, the chlorides should always be used.

59. There are a number of rare elements that are not treated here. As many of the rare elements have only

lately been discovered, and their reactions have not been thoroughly studied, it is impossible to treat them in a Paper of this kind at the present. It has lately been discovered that some of the substances here treated as elements are really composed of two or more closely related elements; but, as they have not yet been separated and studied, it is only possible at the present time to treat them as elements. It is altogether probable that the chemistry of the rare elements will be changed very materially within the next few years.

THE SPECTROSCOPE.

ITS USE IN ANALYSIS.

60. In studying the reactions of the metals, the color that is imparted to the flame by the vapors of many of them is made use of in recognizing them; and in several cases in this Paper the spectrum of the metal is spoken of. In every case where a color is imparted to a flame, the reaction becomes much more distinctive if the spectroscope is used. The spectroscope is made in several forms, but the principle is the same in all. We have seen, in Art. **145,** *et seq.*, *Physics*, that, when light passes through a glass prism, it is separated into its primary colors, and each color is refracted, forming a certain angle with the incident ray. Upon this principle, which is explained in Art. **150,** *et seq.*, *Physics*, the spectroscope is constructed. A common form of spectroscope is shown in Fig. 1. It consists of a tube *a*, at the end of which there is a narrow slit through which the light passes to a lens in the tube, which throws it on the flint-glass prism *b* in the form of a narrow band, owing to the narrow slit through which it has passed. This prism refracts the light at a certain angle, depending on its color, and this line of refracted light is viewed through the tube *c*, which contains a lens and acts as a telescope. The spectroscope is usually supplied with a tube *d*, containing a scale that may

be thrown into the spectrum by the light *e* at the end of the tube. By this means, the spectrum, when viewed through the tube *c*, appears in connection with the scale, so that the exact position of the lines may be noted. The lines produced by any metal always appear in exactly the same place

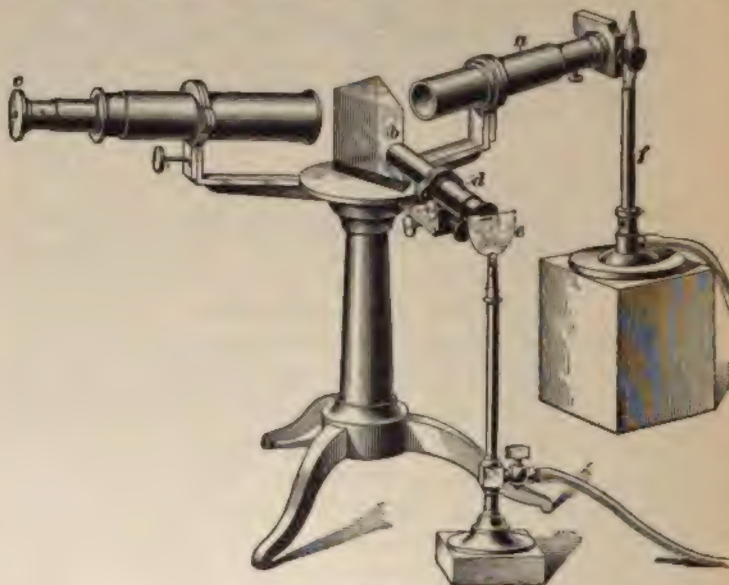


FIG. 1.

when the same instrument is used. The instrument is generally mounted on a brass support, as shown in the figure. The whole of the spectrum cannot be seen at once; hence, the tube *c* is made so that it may be turned, bringing the different parts of the spectrum successively into view. In some instruments the tube *c* is made stationary, and the prism is so arranged that it may be rotated, thus accomplishing the same object. The prism is usually enclosed in a metal covering, through which the ends of the tube *a*, *c*, and *d* pass.

If the Bunsen burner *f* is burning with a non-luminous flame, the spectrum appears blank and is devoid of lines, but if a little sodium compound is brought into the flame it at once assumes a yellow color, and a bright-yellow line is

seen in the spectrum. This is such an extremely delicate reaction that $\frac{1}{3000000}$ part of a milligram of sodium may be detected with accuracy by this means. It is such a delicate reaction that it is difficult to obtain a flame that will not give this yellow line, owing to the sodium floating in the air in the form of dust. The colors imparted to the flame by most of the metals are not single colors, but combinations of different colors. Thus, the violet flame of potassium contains red and violet rays, and produces a dark-red line near one end of the spectrum and a violet line near the other. The red line is much the stronger of the two, and if only a very little potassium is present, the violet line is very faint or may not be seen at all. In the same way the lithium flame, which appears bright red, contains some yellow rays, and its spectrum consists of a bright-red line and a faint-yellow line. As the tube *c* contains a lens and acts as a telescope, it should always be focused before using, so that the lines of the spectrum appear perfectly clear and distinct. No two metals impart exactly the same color to the flame; hence, the spectrum of each is absolutely distinct, as regards the position of its lines. For this reason, when several metals are brought into the flame at once, either in the solid form or in solution, the spectra in no wise interfere with one another, provided the slit in the tube *a* is made narrow enough for the colors to appear as mere lines rather than as bands; in this way, several metals may be detected at once with absolute certainty. For instance, sodium, potassium, and lithium often occur in very small quantities in mineral waters, and the spectroscope is used in detecting them. For this purpose a little pure hydrochloric acid is added, and the water is evaporated nearly to dryness. A drop of this concentrated solution is held in the flame on the loop of a clean platinum wire, and the flame examined by the spectroscope. If the water contains these three metals alone, the spectra will appear as shown in Plate I. If only these three metals are present in the solution, their spectra will appear as shown in the illustration, and no other lines will be seen; but usually the water contains other metals, and these may be determined

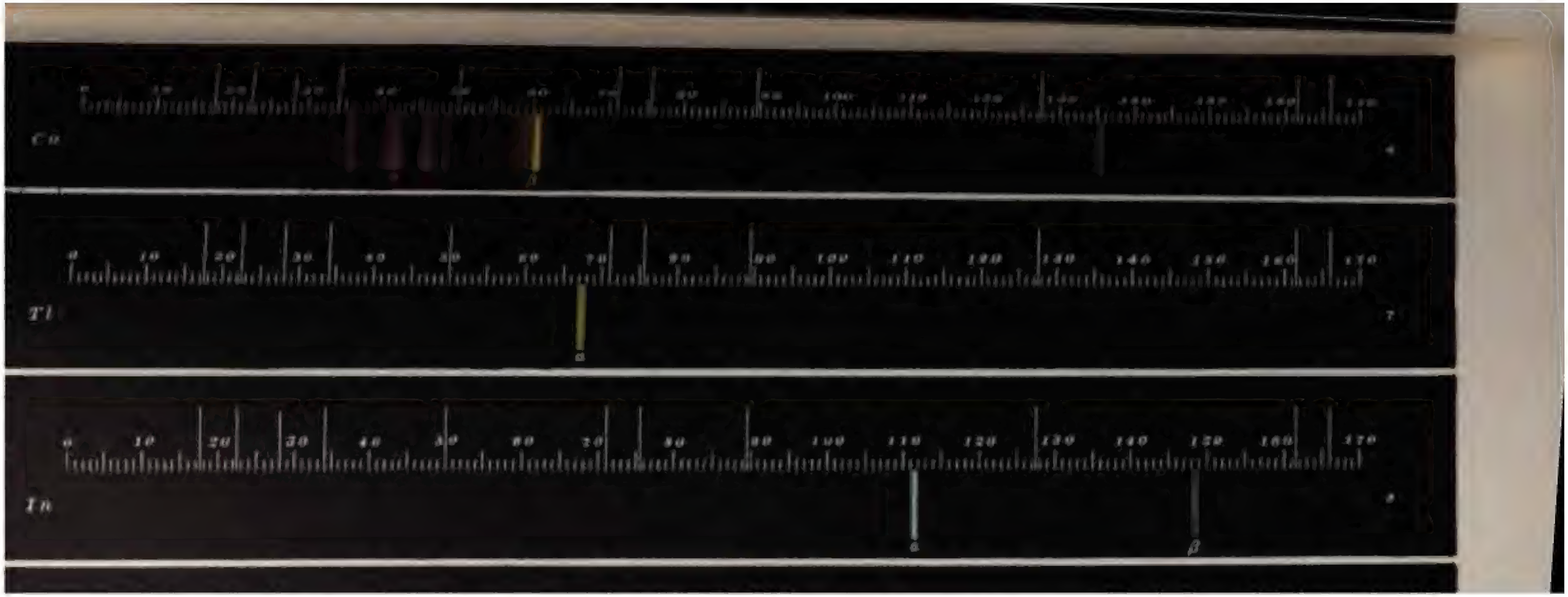
at the same time, by comparing the lines observed with those produced by other metals, as shown in Plate II.

It has been stated that the colors imparted to the flame are due to highly heated vapors; hence, volatile compounds must be used in working with the spectroscope. The chlorides of the metals are generally the most volatile, and nitrates rank next. Carbonates are usually difficult to volatilize, but are easily changed to chlorides by means of hydrochloric acid. Silicates must be decomposed by means of a flux, usually sodium carbonate, and some substances should be held in the reducing flame and then dipped in hydrochloric acid, thus forming chlorides. In the case of very volatile compounds, such as lithium and thallium chlorides, the spectrum, although lasting only a short time, is very brilliant.

61. In Plate II the spectra of the metals that are often determined by means of the spectroscope are given. As the flame is colored by highly heated luminous vapors, metals that do not ordinarily color the flame, if heated to a temperature high enough to volatilize them, impart colors to the flame and consequently produce spectra by which they may be recognized. But in all such cases the wet reactions suffice for the determination of these metals, and it is much easier and simpler to determine them in this way than it is to get the heat necessary to volatilize them. Hence, the use of the spectroscope in analysis is usually restricted to the determination of the alkalies, a few of the rare elements that are easily volatilized, and, in some cases, barium, strontium, and calcium.

ANALYSIS OF WATER.

62. As water is never pure, unless specially prepared, but always contains some substances in solution, the quality of the water depends upon the quantity of these substances contained in it; hence, a quantitative analysis is usually required to determine the fitness of a water for drinking and cooking purposes. But for many purposes all that is required is a qualitative examination, and by this means we



Cs
6
Tl
7
In
8

can learn much of the fitness of a water for drinking purposes by noting whether much or little of the various constituents are present, as indicated by the production of a mere coloration, a slight, or a copious, precipitate, when the reagents are added. In this way, after some practice, quite an accurate opinion can be formed in regard to the amounts of substances present, and the consequent character of the water. In the case of poisonous substances, whose mere presence is sufficient to condemn the water, their qualitative determination alone is required.

63. Treatment of the Sample.—There are several methods of proceeding with the analysis of water, and all methods are modified to suit the particular case. In choosing his mode of procedure, the chemist should be governed largely by circumstances. If something is known of the source and character of the water, the method of analysis should be made to suit the particular case. A method that is very commonly employed is as follows: If the water is clear, about 1 liter is taken for the analysis, and is evaporated in a large, perfectly clean porcelain dish, adding in successive portions, if necessary, until all is in the dish, and then evaporating until the bulk is reduced to about 250 cubic centimeters. During this evaporation, as a rule, a precipitate will be formed, consisting of the metals that were held in solution by free carbonic acid, or in the form of bicarbonates. Allow the dish and contents to cool, and filter through a perfectly pure filter, bringing as much of the precipitate as possible on to the paper. Add a small amount of pure, recently distilled water to the dish, and, after washing out the dish with it, pour it on to the filter, thus washing the part of the precipitate that has been brought on to the paper. Repeat this two or three times, and then proceed to examine the precipitate and the filtrate.

64. Examination of the Precipitate.—The precipitate usually contains some of the following constituents: calcium carbonate, magnesium carbonate, ferric hydrate which is precipitated by boiling a solution of ferrous carbonate,

silica, calcium phosphate, ferric phosphate, ferric silicate, and, sometimes, calcium sulphate, if the water contains much of this substance.

Place the porcelain dish, which still contains much of the precipitate, under the funnel, break the point of the filter with a clean glass rod or platinum wire, and wash the precipitate into the dish with a small quantity of hot, dilute hydrochloric acid. At this point, effervescence is usually observed, due to the escape of carbon dioxide, when the carbonates are decomposed by the acid. Heat the dish and contents to complete the solution as far as possible, and proceed as follows:

1. Take a small portion of the solution, which often is not quite clear, in a test tube or on the lid of a porcelain crucible, and add a few drops of potassium sulphocyanide. A red coloration shows the presence of iron.

2. Evaporate the rest of the solution to dryness on a water bath, in a small porcelain dish. A water bath for this purpose may be made by placing the porcelain dish on a beaker, or other suitable vessel, containing water, as shown in Fig. 2, and heating the water to boiling. The steam from the boiling water, coming against the bottom of the dish, evaporates the solution quite rapidly. A piece of folded paper or some other substance should be placed over the edge of the beaker, to make a small space between the beaker and the dish, for the escape of steam, and the water in the beaker must be replenished as it evaporates. When the solution in the dish is evaporated

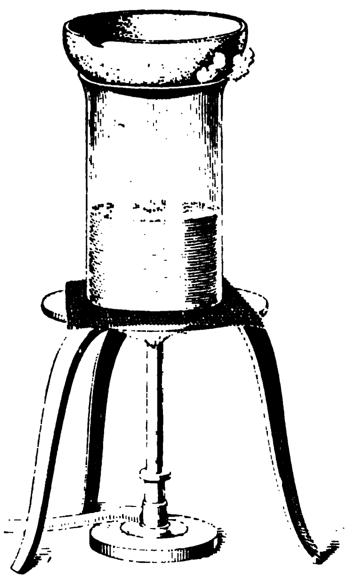


FIG. 2.

to dryness, moisten the residue with hydrochloric acid, heat it gently, add water, and continue the heating until the soluble portion is dissolved. If an insoluble residue remains, it can only be silica, but may be further tested with hydrofluoric acid, if desired.

3. Evaporate a few cubic centimeters of the filtrate nearly to dryness in a test tube, add a few drops of nitric acid, and test for phosphoric acid with ammonium molybdate.

4. To another small portion in a test tube, add a few drops of hydrochloric acid, boil, and then add a little barium-chloride solution. A white insoluble precipitate shows the presence of sulphuric acid.

5. Heat the remainder of the solution to boiling, and add ammonia in sufficient quantity to render the solution alkaline, but avoid a large excess. If a precipitate is formed, filter, and examine the precipitate for iron and aluminum by methods previously described. Heat the clear filtrate to boiling, add from 3 to 5 cubic centimeters of ammonium oxalate, and a like amount of ammonium hydrate; boil for a few seconds, and stand aside for 4 or 6 hours. A white precipitate shows the presence of calcium, which was present in the water in the form of bicarbonate, or also of sulphate, if the portion just tested contained sulphuric acid.

6. Filter off the calcium oxalate, and evaporate the filtrate to a small bulk, if necessary, after making sure that all the calcium was precipitated. To the concentrated filtrate, add about 5 cubic centimeters of a solution of sodium-ammonium phosphate (microcosmic salt), and then about half its volume of ammonia; stir well, and stand in a cool place for 10 or 12 hours. A white precipitate shows the presence of magnesium, which was in the water in the form of carbonate or bicarbonate. The precipitate sometimes adheres to the sides of the beaker in the form of colorless crystals that cannot be seen until the liquid is poured out.

65. Examination of the Filtrate.—1. To about 10 cubic centimeters of the filtrate, add 1 or 2 cubic centimeters of nitric acid, and, after mixing thoroughly, add silver

nitrate, when chlorine, if present, will be precipitated as white silver chloride. This is sufficient proof of chlorine, but, if any considerable precipitate is formed, it may be confirmed by dissolving in ammonia, and reprecipitating with nitric acid.

2. To another portion of about 10 cubic centimeters, add 1 cubic centimeter of nitric acid, evaporate the whole to about one-half cubic centimeter, and test for phosphoric acid with ammonium molybdate.

3. Evaporate about 30 cubic centimeters of the filtrate to a small bulk, and test its reaction with litmus paper. If the reaction is alkaline, and a drop or two of it, placed on a watch glass, effervesces when brought in contact with a drop of acid, and, if calcium carbonate is precipitated when calcium chloride is cautiously added to a portion of the alkaline solution, the water contains a carbonate of an alkali metal. Evaporate the rest of this test to dryness on the water bath, boil the residue with alcohol, filter, evaporate the filtrate to dryness, dissolve the residue in a very little water, and test this solution for nitric acid with diphenylamine or aniline sulphate.

A diphenylamine solution is made by treating about 2 milligrams of the crystals with 5 cubic centimeters of concentrate sulphuric acid, adding an equal volume of water, and mixing the solution thus formed with about 5 cubic centimeters of concentrate sulphuric acid. To test for nitric acid, place about half a cubic centimeter of this solution on a watch glass, and add a drop or two of the liquid to be tested. If nitric acid is present, a blue line will be formed where the liquids meet.

The aniline-sulphate solution is made by adding about half a dozen drops of aniline to 15 cubic centimeters of dilute sulphuric acid, and then adding this solution drop by drop to about 40 cubic centimeters of concentrate sulphuric acid. If about 1 cubic centimeter of this solution is placed on a watch glass, and a drop or two of a liquid containing nitric acid is added, a red color is produced.

Very often a drop or two of the original water, or of a

somewhat concentrated solution, is added to one of these reagents, to test for nitric acid; but the method described, although rather long, is usually to be recommended on account of its greater accuracy.

4. To the remainder of the original filtrate, add about 5 cubic centimeters of hydrochloric acid, and evaporate at first over the Bunsen flame, and finally to dryness on the water bath. Moisten the residue with hydrochloric acid, warm gently, add water, bring into solution by the aid of heat, and filter off the insoluble silica, which is nearly always present. To a little of this filtrate in a test tube, add a few drops of hydrochloric acid and then barium chloride. A white insoluble precipitate shows the presence of sulphuric acid. Render the rest of the filtrate distinctly alkaline with ammonia, add about 5 cubic centimeters of ammonium oxalate, bring to boiling, add 1 or 2 cubic centimeters of ammonia, and stand in a warm place for about 5 hours for the precipitate to collect and settle. A white precipitate shows the presence of calcium. Filter, and test a portion of the filtrate for magnesium, by ammonia and sodium-ammonium phosphate, as previously described. The rest of the solution is tested for the alkalies. This may be done in several ways. The shortest, and probably the most satisfactory, method of testing is to evaporate the solution nearly to dryness, holding a drop of it in the non-luminous flame, and noting the color imparted by the solution, using the blue glass, or, still better, examining the flame by means of the spectroscope. In case a spectroscope is not accessible, it may be necessary to adopt another method for potassium. Sodium is always recognized by the yellow color it imparts to the flame, but, in the presence of large quantities of sodium, a small amount of potassium may be overlooked, even when the flame is examined through a blue glass; hence, in the presence of much sodium, if no potassium is found by the flame reaction, the following method should be employed:

Evaporate the test to dryness, and heat it carefully over the flame until all ammonium compounds are volatilized. Heat the residue with from 10 to 30 cubic centimeters of

about 50 cubic centimeters have passed over, remove the cylinder and add 1 or 2 cubic centimeters of Nessler's solution. A yellow color at this point shows the presence of free ammonia. Continue the distillation until about 200 cubic centimeters of the water have passed over. Then remove the light and add 50 cubic centimeters of a solution of potassium hydrate and potassium permanganate.* Return the burner, and continue the distillation. When 50 cubic centimeters of the water have passed over, add 2 cubic centimeters of Nessler's solution. A yellow color shows the presence of albuminoid ammonia, but the absence of a yellow color does not prove its absence. If albuminoid ammonia is present, some of it nearly always comes over with the first 50 cubic centimeters of the distillate, but we cannot state positively that the water contains no albuminoid ammonia until three portions of the distillate, of 50 cubic centimeters each, have been tested in this manner.

68. Nitrous Acid.—To test for nitrous acid, it is usually sufficient to measure 50 cubic centimeters of the water into a suitable vessel, add 1 cubic centimeter of dilute sulphuric acid, 1 cubic centimeter of potassium-iodide solution, and a little starch solution. The formation of a blue color, either at once or after a few moments, indicates a relatively large amount of nitrous acid, but, if the color does not appear for some time it indicates that only a small quantity is present, while a failure to obtain a blue color, even after several hours, indicates that the water is free from nitrous acid.

In performing this operation, bright daylight, and especially direct sunlight, should be avoided, or a blue color will probably be produced even if no nitrous acid is present. And it is best to treat 50 cubic centimeters of a water, known to be free from nitrous acid, in the same manner and at the

* To make this solution, dissolve 50 grams of potassium hydrate and 2 grams of potassium permanganate in 250 cubic centimeters of water. Boil until about one-fourth of the liquid is evaporated, in order to drive off any ammonia that may be present, and then add enough water, which is strictly pure and free from ammonia, to make 250 cubic centimeters of solution.

same time that the water to be tested is treated. This method is very simple, and its results are quite reliable, but not absolutely certain, as the water may contain substances that interfere with the reaction. To avoid this source of error, we may place about 300 cubic centimeters of the water to be examined in a retort or flask, add a little acetic acid, and distil it as in the preceding article, in testing for ammonia. Nitrous acid, if present, will come over in the first 50 cubic centimeters of the distillate, and this may be tested with potassium iodide and starch solution as just described, or still better with a solution of sulphanilic acid and naphthylamine in acetic acid. To make this solution, dissolve one-half a gram of sulphanilic acid in 150 cubic centimeters of acetic acid. Then boil one-tenth of a gram of naphthylamine with 20 cubic centimeters of water, and decant the colorless liquid, from the violet-colored residue, into 150 cubic centimeters of acetic acid. Mix these two solutions, and, if the resulting mixture is colored, add zinc dust, and shake till the color is destroyed. Allow the solution to settle, decant the clear liquid, and keep it in a well stoppered bottle.

If a little of this solution is added to the distillate, and the mixture heated to 70° or 80°, it will assume a rose color if nitrous acid is present.

69. Organic Matter.—To test for organic matter in water, it is usually sufficient to evaporate about 200 cubic centimeters of the original sample to dryness on the water bath, and heat the residue over the Bunsen burner, gently at first, and gradually increasing the temperature. If there is any considerable amount of organic matter present, the residue will become brown or black, and a burnt odor is generally observed. If the water contains carbonates, and the residue has not been heated too strongly, carbon dioxide with a burnt odor will generally be given off when the residue is treated with dilute hydrochloric acid.

70. Decaying Matter.—A simple test for decaying organic matter may be made by filling a rather large bottle

to two-thirds its capacity with the water to be tested, covering it with the hand, shaking it well, and noting if any odor is evolved. If hydrogen sulphide is present, it will probably mask any other odor. In this case place a fresh sample of the water in the bottle, add a little copper sulphate, cover with the hand, shake well, and note the odor.

If hydrogen sulphide is found in applying this test, we should seek to confirm it by means of reagents, although it often happens that the odor evolved is a more delicate test than any of the wet reactions. To test water in the wet way for hydrogen sulphide, nearly fill a rather large white bottle with the water to be tested, and add a few drops of a strong solution of lead acetate in sodium hydrate. If this produces a white precipitate, a few drops of a strong solution of copper chloride in water must be substituted. Place the bottle on a sheet of white paper, and look down through it towards the white surface. If a black precipitate or a brown coloration is produced by either of these reagents, it shows the presence of hydrogen sulphide in greater or less amount.

This coloration may be produced either by free hydrogen sulphide dissolved in the water or by the sulphide of an alkali; hence, if the water is alkaline, indicating the probable presence of an alkaline sulphide, the following method of distinguishing between the two should be employed: Close a rather large bottle, half filled with the water, with a cork, to the bottom of which is fastened a piece of filter paper that has been saturated with a solution of lead acetate and then moistened with a drop or two of ammonium carbonate. Allow the bottle thus stoppered to stand for several hours, and shake at frequent intervals, taking care not to allow any of the water to spatter on to the paper. Hydrogen sulphide will give the paper a brown color, but the sulphide of an alkali will not affect it unless it comes in contact with the water.

71. Carbonic Acid and Bicarbonates.—To a rather large sample of the freshly drawn water, add a little lime water, a drop at a time. If the water contains free carbonic

acid, a white precipitate of calcium carbonate will be formed at first, and upon stirring will be dissolved by the free carbonic acid, forming calcium bicarbonate; but upon the addition of a few more drops of the lime water, a permanent precipitate of calcium carbonate will be formed. If the water does not contain free carbonic acid, but does contain bicarbonates, a permanent precipitate will be formed at once.

72. Poisonous Metals.—The poisonous metals most frequently found in water are lead, copper, and zinc. To examine the water for these, place about 1 liter of the water in a tubulated retort, and add about 10 cubic centimeters of dilute hydrochloric acid; direct the neck of the retort steeply upwards, leave the tubulure open, and evaporate the water to about 100 cubic centimeters. If a precipitate forms during this concentration, it is filtered off. As it may contain lead, add to it a little tartaric acid, then a slight excess of ammonia, boil, filter, and test the filtrate for lead with hydrogen sulphide. Lead hydrogen sulphide through the first filtrate, to precipitate copper and lead, filter, and, if any considerable precipitate is formed, treat it for the separation of these metals, as described in the separation of the metals of Group II. If only a slight precipitate is formed, more of the water must be evaporated and treated in the same way, in order to get enough of the precipitate, so that it can be separated. Boil the filtrate, or the solution if no precipitate was formed, to expel all traces of hydrogen sulphide, and, if sulphur separates during the boiling, filter it off. To the clear liquid, add a few drops of concentrate nitric acid and 3 or 4 cubic centimeters of ammonium chloride, heat to boiling, and add a slight excess of ammonia. If a precipitate forms, filter it off, and if of any considerable size, examine it for iron and chromium, for iron, if present in any considerable quantity, is injurious to the health, and chromium is quite poisonous.

Add just enough acetic acid to the filtrate to render it acid, and lead a current of hydrogen sulphide through it. A white

precipitate shows the presence of zinc. Or the usual method of analysis may be followed, and ammonium sulphide added instead of acetic acid and hydrogen sulphide.

Arsenic sometimes occurs dissolved in water, and when present should never be overlooked. Marsh's test is nearly always used in examining water for arsenic. It may be performed as described in Art. **74,** *Inorganic Chemistry*, Part 2. Or, a somewhat simpler form of apparatus may be used, as shown in Fig. 3. To test the water for arsenic,

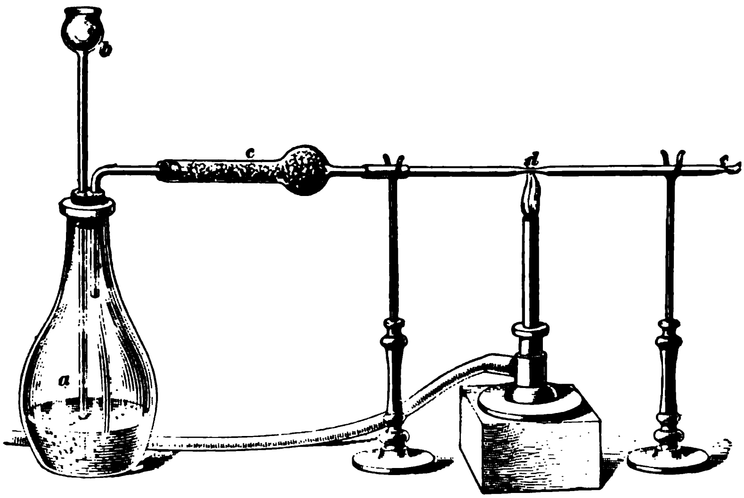


FIG. 3.

pure zinc is placed in the evolution flask *a* and covered with pure water. Connect the apparatus, and pour about half as much concentrate sulphuric acid through the funnel tube *b* as there is water in the flask. The hydrogen evolved passes out through the drying tube *c*, which is filled with granulated calcium chloride, and thence through a hard-glass tube that has been drawn out at a point *d*. After enough hydrogen has been evolved to drive all the air out of the apparatus, so that there is no danger of its containing an explosive mixture of air and hydrogen, bring a Bunsen burner under the tube at *d*, and ignite the hydrogen at *e*. If, after several trials, no

black spot is deposited on a piece of cold porcelain by the flame *e*, and no mirror is deposited on the tube between *d* and *e*, we may assume that our materials are free from arsenic. Now through the funnel tube *b* add a few cubic centimeters of the water that has been concentrated as just described, taking care not to introduce any air with the water, and after a few moments test the flame *e* with a piece of cold porcelain. The tube must be kept at a red heat at *d*, and the flame at *e* must be repeatedly tested for several minutes. If, at the end of fifteen minutes, the flame has not deposited a black spot on the cold porcelain, and no mirror has been formed between *d* and *e*, wė can safely assume that the water is free from arsenic, but if either of these phenomena is observed, it shows the presence of arsenic.

If antimony were present in the water, it would give the mirror in the tube and a black stain on the porcelain, but, as antimony is not likely to occur in water, and as its compounds are also poisonous, it is not necessary as a rule to distinguish between antimony and arsenic. If it is desired to learn which is present, this is easily done, for the stain produced by arsenic is brownish black and has a bright luster, while the stain produced by antimony is a dull deep black. The stain produced by arsenic is immediately dissolved by a solution containing a mixture of sodium hypochlorite and sodium chloride, while the stain deposited by antimony is only dissolved very slowly, or not at all, by this solution.

73. The Water is Turbid.—In case the water to be examined is not clear, part of the tests must be made on the water in its original condition and part after it has cleared. Fill a large bottle with the water, stopper it tightly, and stand it aside in a cool, dark place until perfectly clear. Draw off the necessary quantity of the clear water by means of a siphon, and treat it as described in Arts. **63, 64, 65, 69,** and **71.** Then, using fresh samples of the water in its original turbid condition, test for ammonia as described in Art. **66,** for nitrous acid according to Art. **68,** for decaying matter according to Art. **70,** and for

poisonous metals according to Art. **72.** In the case of turbid waters, the distillation method must be used for nitrous acid.

It is often desirable to know the character of the solid matter in water. In order to learn this, filter off the sediment that remained in the bottle in which the water was set aside to become clear, treat it with hydrochloric acid, filter off the insoluble matter, which nearly always remains, and subject the filtrate to treatment for the group separations. Fuse the insoluble residue with sodium carbonate, dissolve the fusion in hydrochloric acid, and put this solution also through the group separations.

EXAMINATION OF URINE.

74. Urine is the most important vehicle through which waste matter escapes from the body; hence, it always contains salts and organic matter. The constituents of normal urine vary considerably, both in character and quantity, so that, to obtain complete information in regard to the character of a sample of urine, a quantitative examination is required. But certain constituents that are never present in health are found in urine in case of disease; hence, we may learn much from a qualitative examination. The composition of the urine varies at different times in the day; hence, a sample representing the average for twenty-four hours should be taken for analysis. The quantity of urine passed in twenty-four hours varies considerably, but averages from 1,200 to 1,500 cubic centimeters.

75. Color.—The first step in the examination of urine is usually to note its color. In health the color may be light yellow, lemon yellow, or amber. As, in health, the quantity of coloring matter passed remains comparatively constant, while the total amount of urine passed varies greatly, it necessarily follows that the less urine passed, the darker will be its color, owing to the strong solution of

PLATE III.

From Nature by Dr. J. Vogel.

VOGEL'S SCALE OF URINE TINTS.

FROM TYSON'S EXAMINATION OF THE URINE. TENTH EDITION.

coloring matter that is thus obtained. Hence, normal urine may vary considerably in color, but, if very light or very dark colored, disease is indicated. To determine the color of a sample of urine, it is merely necessary to place some of it in a colorless-glass vessel and compare the shade with the colors given in *Vogel's scale of urine tints* in Plate III.

76. Reaction.—Usually the second operation in the examination of urine is to test its reaction with litmus paper. Normal urine should be slightly acid, but shortly after a meal it may be neutral or even slightly alkaline. The total urine passed in twenty-four hours should surely have an acid reaction; if alkaline, it shows that the urine has decomposed before passing, and consequently indicates a deranged condition of the system. Urine containing much albumin is often alkaline; hence, if a sample of urine is alkaline, this is taken as an indication of Bright's disease. To test the reaction of urine, two pieces of litmus paper should be used, one red and the other blue. As the reaction is usually only faintly acid or alkaline, the paper should not be strongly colored, or the urine may not be strong enough to change the color. With paper that is only faintly colored the reaction is much more delicate. The urine should not be allowed to stand longer than necessary before taking its reaction, as it is likely to decompose, especially if it stands in a warm place, and a urine that is originally acid may thus become alkaline.

77. Specific Gravity.—As urine is a solution of solid substances in water, it is always heavier than water. The specific gravity depends on the amount and character of the solid matter passed, and upon the quantity of urine. The amount of solid matter will be the same whether a large or a small amount of urine is passed; hence, if the quantity of urine is small, the solution will be concentrate, and the specific gravity high, while, if the quantity of urine is large, the solution will be dilute, and the specific gravity will consequently be low. In health the specific gravity of urine may vary from 1.005 to 1.025; while in case of disease it

varies from 1.002 to 1.060. Sugar, which is present in the urine in case of diabetes, gives it a high specific gravity. Hence, if the specific gravity is more than about 1.028, the urine should at once be tested for sugar. The test for specific gravity is usually made with a hydrometer, which is graduated from 1.000 to 1.060, known as a *urinometer*. To make this test, a sample of urine is placed in a cylinder, and the urinometer is lowered into it, as shown in Fig. 4. The urinometer will sink into the urine up to some point on the graduated stem, and the reading on the stem at the surface of the liquid is the specific gravity. The urinometer is just like the hydrometer described in Art. **42,** *Physics*, except that it is graduated from 1.000 to 1.060, and many urinometers contain a thermometer in the stem. All of them are made to take the specific gravity of the urine at a certain temperature, generally 15°, and, as the urine is usually warmer than this, it must be cooled to this temperature before it is tested. This may readily be done by holding the cylinder containing the urine in cold water, or by allowing cold water to run over the outside of the cylinder; but care must be taken not to allow any water to get into the urine, or its specific gravity will be reduced. The urinometer is nearly always used in taking the specific gravity of urine, on account of the ease and rapidity with which it yields a result; but if there should be an error in the graduation of the urinometer, all results obtained with it would be erroneous; hence, when great accuracy is desired, the specific gravity is also taken by means of a bulb, or specific-gravity bottle, as described in Art. **36,** *Physics*.

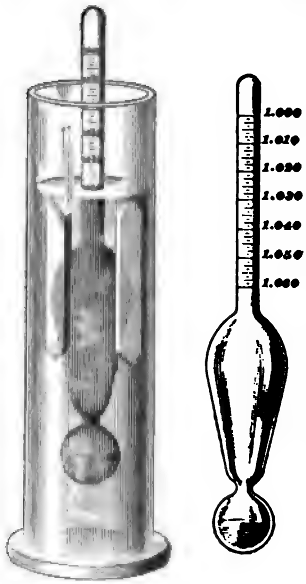


FIG. 4.

From the specific gravity of urine, the approximate quantity of solid matter that it contains may be calculated. The last two figures of the specific gravity multiplied by $2\frac{1}{3}$ gives the approximate weight, in grams, of solid matter in 1 liter of the urine.

ILLUSTRATION.—The specific gravity of a sample of urine is 1.010. To find how much solid matter it contains, multiply 10 by $2\frac{1}{3}$; thus, $10 \times 2\frac{1}{3} = 23\frac{1}{3}$ grams in 1 liter. If the amount of urine passed in 24 hours is known, the approximate quantity of solid matter passed may readily be found from this result, by a simple calculation.

78. Sugar.—Sugar is found in the urine of patients suffering from diabetes, and urine containing sugar is frequently spoken of as diabetic urine. Sugar occurs in urine in the form of *glucose*, or *grape sugar*. It probably never occurs in normal urine, and certainly never in any considerable amount; hence, if sugar enough to give a distinct reaction is found in urine, it is a certain indication of disease. There are several methods of testing for sugar in urine, but probably Fehling's solution is most commonly employed for this purpose.

1. *Determination by Fehling's Solution.*—Fehling's solution is an alkaline solution of copper. To make it, dissolve 34.652 grams of pure crystallized copper sulphate in sufficient water to make 500 cubic centimeters of solution, and keep in a well stoppered bottle. Then dissolve 173 grams of pure crystallized neutral sodium tartrate in 480 grams of a solution of sodium hydrate, having a specific gravity of 1.14; dilute to 500 cubic centimeters, and keep this solution also in a well stoppered bottle. These solutions are mixed in equal proportions just before using, but must be kept in separate bottles until they are to be used, as decomposition takes place when they are mixed and allowed to stand. To use the Fehling solution, pour 1 cubic centimeter of the solution of sodium tartrate and sodium hydrate into a rather large test tube, add an equal amount of the copper-sulphate solution, dilute this to 10 cubic centimeters, and heat to boiling. If the solution has been prepared according to the directions given, it should remain clear; if a precipitate

forms, the solution is useless, and a new one must be made up. If the chemicals used in preparing the solution are pure, and it is prepared as directed, it will remain clear. After boiling the solution for a few seconds, remove it from the flame, and at once add the urine to be tested, a few drops at a time. When about 1 cubic centimeter of the urine has been added, the mixture should again be heated to boiling, but the boiling must not be continued more than a few seconds. Continue the gradual addition of the urine, keeping the solution as near the boiling point as practicable, until 10 cubic centimeters have been added, and again boil the solution for a few seconds. If the solution remains unchanged after this treatment, it is quite safe to assume that the urine is free from sugar, for sugar when present acts as a reducing agent, destroying the color of the solution, and precipitating red cuprous oxide Cu_2O. If any considerable amount of the red cuprous oxide is precipitated, it is proof of the presence of sugar. In experienced hands this is a very accurate test, but, like other tests for sugar in urine, it only yields reliable results when properly performed. Hence, the beginner should always confirm his results, by repeating the determination or by another test.

2. *Trommer's Test.*—To 8 or 10 cubic centimeters of the urine in a large test tube, add one-third of its bulk of sodium hydrate, made by dissolving 10 grams of solid sodium hydrate in 30 cubic centimeters of water, and then add, a drop at a time, a solution of copper sulphate, made by dissolving 5 grams of the pure crystals in 50 cubic centimeters of water. After the addition of each drop of the copper sulphate, the solution should be shaken, and if the precipitate at first formed dissolves, this is evidence of sugar, but is not conclusive. Continue the addition of copper sulphate until a slight permanent precipitate is formed, and then heat the solution just to the boiling point, and remove it at once from the flame. If sugar is present, a precipitate of yellow cuprous hydrate is formed. This soon changes to red cuprous oxide, which settles to the bottom or sides of the tube.

One of these methods is nearly always used in testing for

sugar in urine, but care must be taken in using them, or erroneous results will be obtained. If the boiling is continued long when the copper solution is added, it may be decolorized, or a slight precipitate may even be formed when the urine does not contain sugar, as other constituents of the urine have the power of reducing copper sulphate, when boiled with it for some time. Albumin, if present, interferes with the reduction of copper; hence, it must be removed, by one of the methods given later, before one of these methods can be employed. To avoid these sources of error, the following exact method is sometimes used:

3. *Brücke's Method.*—To 50 cubic centimeters of the urine in a beaker, add 60 cubic centimeters of a solution of neutral lead acetate, made by dissolving 6 grams of the solid lead acetate in sufficient water to make 60 cubic centimeters of solution. This precipitates most of the substances that would interfere with the reaction, and leaves the sugar in solution. Filter, wash the precipitate on the filter once or twice with cold water, and to the filtrate add ammonia, in slight, but distinct, excess. This precipitates the sugar as lead saccharate $(PbO)_2(C_6H_{12}O_6)_2$. Allow the precipitate to settle, wash twice by decantation with cold water, then filter and wash on the filter with cold water until the washings give no reaction with red litmus paper. Wash the precipitate from the filter into a beaker, using about 75 cubic centimeters of water, and pass a current of hydrogen sulphide through the liquid in which the precipitate is suspended, as long as a black precipitate of lead sulphide is formed. The hydrogen sulphide breaks up the lead saccharate, precipitating the lead as sulphide, and the sugar goes into solution. Filter off the lead sulphide, and wash the precipitate two or three times with cold water. Boil the filtrate until all hydrogen sulphide is expelled, and the volume of the liquid is reduced to about 50 cubic centimeters. If any sulphur separates in the solution during the boiling, filter it off, and stand the clear liquid aside for at least twenty-four hours for any uric acid that it may contain to separate in crystals. A little of the clear liquid, which is now freed from substances that

forms, the solution is useless, and a new one must be made up. If the chemicals used in preparing the solution are pure, and it is prepared as directed, it will remain clear. After boiling the solution for a few seconds, remove it from the flame, and at once add the urine to be tested, a few drops at a time. When about 1 cubic centimeter of the urine has been added, the mixture should again be heated to boiling, but the boiling must not be continued more than a few seconds. Continue the gradual addition of the urine, keeping the solution as near the boiling point as practicable, until 10 cubic centimeters have been added, and again boil the solution for a few seconds. If the solution remains unchanged after this treatment, it is quite safe to assume that the urine is free from sugar, for sugar when present acts as a reducing agent, destroying the color of the solution, and precipitating red cuprous oxide Cu_2O. If any considerable amount of the red cuprous oxide is precipitated, it is proof of the presence of sugar. In experienced hands this is a very accurate test, but, like other tests for sugar in urine, it only yields reliable results when properly performed. Hence, the beginner should always confirm his results, by repeating the determination or by another test.

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would interfere with the reaction, is decanted, or filtered off, and tested with Fehling's solution, as previously described.

79. Albumin.—Whether albumin ever occurs in strictly normal urine or not, is a question that has not been settled. But if present in normal urine, it is only in minute quantities, while in case of some diseases, especially Bright's disease, the urine may contain large quantities of it. In testing for albumin, the sample should be perfectly clear, and if the urine is cloudy or contains a sediment, it should be filtered before testing. There are several methods of testing for albumin in urine. Those most frequently used are here given.

1. *Testing by Heat.*—To test for albumin by means of heat, half fill a test tube with perfectly clear urine, and gently heat the upper part of the liquid to a temperature of 75° or 80°, and examine the sample in a good light to see if any difference in transparency between the upper and lower parts of the sample can be observed. If much albumin is present, it is usually precipitated by the heat in the upper part of the tube, while in the lower part, where the sample is still comparatively cool, but little or no precipitation is observed. Now continue heating until it boils, and finally bring the whole sample to boiling. If a precipitate is formed, or the sample becomes turbid, it is due to the presence of albumin or phosphates of the alkaline earths. To distinguish between these, add about half a cubic centimeter of nitric acid, drop by drop, when the precipitate, if it is a phosphate, will dissolve, while albumin is unchanged or may become more distinct.

If the sample of urine tested is strongly alkaline, probably no precipitate will be formed until the nitric acid is added, even though it contains considerable albumin; and, if it is strongly acid, a soluble modification of albumin may be formed that will not be precipitated until the sample is neutralized with sodium hydrate. Hence, we must be governed in our mode of procedure by the reaction of the urine. If the urine is acid to litmus paper, and a sample, when treated

as just described, gives no precipitate, a second quantity, in a test tube, should be neutralized with sodium hydrate, and then treated as directed above.

2. *Heller's Test.*—Heller's test depends upon the coagulation of albumin by nitric acid, when the two liquids are brought in contact without mixing. To make this test, place a few cubic centimeters of strong, colorless nitric acid in a test tube, and add an equal amount of the clear urine to be tested, allowing it to run down the side of the inclined tube, so that it will not mix with the nitric acid. If much albumin is present, a white band will be formed at the point where the two liquids meet, which varies in thickness according to the quantity of albumin present. If a precipitate is not formed at once, the tube and contents should be set aside for several hours.

Some chemists prefer to place the urine in the tube first, and add the acid to it, and this may be done by inclining the tube containing the urine, and pouring the nitric acid carefully down the side of the tube, when the two liquids will form separate layers, and the white ring or band will be formed where they meet. This test is sometimes modified, by getting the two layers as described, and then heating cautiously, taking care not to allow the liquids to mix more than is necessary. As in the case of the test by heat, if the urine is strongly acid, the test by nitric acid may fail to produce a precipitate, even though the urine contains considerable albumin, on account of the formation of so called acid albumin, which is soluble in acids. Consequently, if the urine is acid to litmus paper, and gives no reaction for albumin by Heller's test, as just described, a fresh sample of it should be neutralized with sodium hydrate, and the test repeated on this neutral sample.

When nitric acid stands in contact with urine, it acts on the coloring matter, forming a dark ring that grows darker on standing, and if albumin is present, and coagulated by the nitric acid, it is often colored more or less by these coloring matters, which have been rendered dark by the acid.

3. These tests have been modified in a number of ways

by different chemists. A very good method is as follows: Fill a test tube to about one-third its capacity with the clear urine to be tested, and heat it to the boiling point; remove it from the flame, and, without allowing it to cool, pour about 1 cubic centimeter of colorless nitric acid down the side of the inclined tube, so that it forms a separate layer. If a white band does not form after standing for some time, heat the solution carefully at first, so that the two liquids remain separate, and finally shake them up so that the acid is thoroughly mixed with the urine, and allow the tube to stand for several hours.

As albumin is rather difficult to determine, and in many cases is very important, a single test should never be relied on; but, if two of the tests given are used, and the reaction of the urine taken into account, it is scarcely possible to make a mistake.

The determinations given are the principal qualitative tests applied to urine, but it occasionally happens that qualitative determinations of sulphuric, hydrochloric, and phosphoric acids are required. For these constituents the following tests are recommended:

80. Sulphuric Acid.—Sulphuric acid occurs in normal urine combined with sodium and potassium, forming sulphates of these metals. Normally, about 2 grams of sulphuric acid are passed daily. To determine sulphuric acid, place about 25 cubic centimeters of the urine to be tested in a small beaker, add about 1 cubic centimeter of concentrate hydrochloric acid, and then 8 or 10 cubic centimeters of barium-chloride solution, and stir well. A white precipitate shows the presence of sulphuric acid. Something may be learned of the quantity of sulphuric acid present by this reaction. If the solution becomes milky, it shows that the urine contains about the normal amount of sulphuric acid, while a creamy appearance and consistency shows an increase, and a mere cloudiness a decrease, in the quantity. Hydrochloric acid must always be added before the barium chloride, or barium phosphate may also be formed. If the urine is

not clear, or if a precipitate is formed when the hydrochloric acid is added, it must be filtered and the clear filtrate tested for sulphuric acid.

81. Hydrochloric Acid.—Hydrochloric acid occurs in urine chiefly combined with sodium, in the form of sodium chloride, but also in smaller quantities, combined with potassium and ammonium. In normal urine, the amount passed in 24 hours should contain from 10 to 16 grams of chlorides. To test for hydrochloric acid, place about 25 cubic centimeters of the clear urine in a small beaker, add about half a cubic centimeter of dilute nitric acid to keep the phosphates in solution, and then 2 or 3 drops of silver-nitrate solution. If the urine contains from $\frac{1}{2}$ to 1 per cent. of chlorides, this will form curdy lumps of white silver chloride which do not readily break up, or else give the solution a milky appearance when it is gently agitated. If curdy lumps of precipitate are not formed, but the solution becomes equally milky throughout, it shows that the urine contains less than the normal amount of chlorides, while a failure to get a precipitate shows the absence of chlorides.

A small amount of albumin in the urine does not usually interfere with the determination of the normal quantity of hydrochloric acid, but if much albumin is present, or if the quantity of hydrochloric acid is small, it is necessary to remove the albumin before testing for hydrochloric acid. To do this, heat the sample of urine to boiling, add a few drops of nitric acid, allow the albumin thus precipitated to settle, and filter it off. To the clear filtrate add a little more nitric acid, and then silver nitrate, as just directed. This determination is sometimes important in the case of certain acute diseases. In these cases the disappearance of chlorides from the urine indicates a change for the worse, while their reappearance always denotes improvement. In the case of acute pneumonia, the appearance of chlorides in the urine is frequently the first indication of recovery.

82. Phosphoric Acid.—Phosphoric acid is contained in urine in the form of calcium and magnesium phosphates

(known as earthy phosphates), and alkaline phosphates, principally acid sodium phosphate. There are two common methods of determining the phosphates:

1. Place in a small beaker about 25 cubic centimeters of the urine to be tested, render it slightly, but distinctly, alkaline with ammonia, heat gently until a precipitate begins to form, stir well, and stand aside for an hour or so, for the precipitate to collect and settle, taking care that the solution remains alkaline. If earthy phosphates are present, they will be precipitated from this alkaline solution. If the urine is normal, the precipitate will be white; but if abnormal coloring matters are present, they will be precipitated with the phosphates, and give their color to the precipitate. The precipitate of earthy phosphates is filtered off, and the filtrate is tested for alkaline phosphates. To do this, add from 5 to 8 cubic centimeters of magnesium solution,* stir well, and stand aside for a few moments. Then stir again, and note the appearance of the sample. The phosphoric acid of the alkaline phosphates is precipitated as pure white magnesium-ammonium phosphate; and, if the liquid has a milky apearance, a normal amount of phosphoric acid is present. If the liquid is more creamy in appearance, it shows an excess of phosphoric acid, while a mere cloudiness shows a decreased amount. If no precipitate or only a slight one is formed, the solution should be allowed to stand for several hours and then be again examined.

It frequently happens that the total phosphoric acid is all that is required. In this case, place about 25 cubic centimeters of the urine in a small beaker, render it alkaline with ammonia, heat gently, and slowly add about 8 cubic centimeters of magnesium solution, with constant stirring.

2. We have seen that silver nitrate precipitates phosphoric acid from neutral solutions, and this fact is sometimes made use of in determining phosphoric acid. This is done

* To make magnesium solution for this purpose, dissolve 1 gram of magnesium sulphate in 8 cubic centimeters of water, add 1 gram of ammonium chloride and, when all is dissolved, add 1 cubic centimeter of concentrate ammonia.

as follows: Place about 25 cubic centimeters of the sample in a beaker, add about 1 cubic centimeter of nitric acid, and precipitate the hydrochloric acid with an excess of silver nitrate. Stir well, and filter off the silver chloride. The filtrate contains the phosphoric acid in acid solution, together with the excess of silver nitrate added to precipitate the hydrochloric acid. To the clear filtrate, add ammonia, drop by drop, with constant stirring, until the neutral point is just reached, when silver phosphate is precipitated. As silver phosphate is soluble in ammonia, a few more drops will dissolve it, and from this solution it may be reprecipitated by adding nitric acid, a drop at a time, until the solution is just neutral. If it is desired to do so, the earthy phosphates may be removed by heat and ammonia. The filtrate is rendered acid, and the alkaline phosphates determined by this method. As this test only yields good results when carefully and properly applied, the first method is recommended, especially for beginners, but it is a good plan to confirm the results thus obtained by the second method.

83. Samples for Practice.—In examining urine for sugar and albumin, only negative results are ordinarily obtained; hence, the student is advised to make up samples containing these substances, in order to become familiar with their reactions. This may be done by dissolving small quantities of these substances in water, and adding these solutions to samples of normal urine. A solution containing sugar may readily be made by dissolving about 1 gram of grape sugar, or glucose (the kind of sugar that occurs in urine), in 50 cubic centimeters of water, and adding this to an equal amount of urine. A solution containing albumin is not quite so easily prepared, but may be made quite readily as follows: Add the white of an egg to about 100 cubic centimeters of cold water, stir it well for some time, and allow the part that does not dissolve to settle. After the undissolved portion has completely subsided, pour the clear liquid, which contains albumin in solution, into an equal volume of urine.

COMMON INORGANIC POISONS.

84. The chemist is often called upon to determine if a substance contains a certain poison, and this section is designed to enable the student to answer such a question, and to give him a certain familiarity with the methods employed in such cases. Obviously, an exhaustive treatment of the subject of poisons would be out of place in a Paper of this character, hence, only the common poisons will be treated. But, if the student makes himself familiar with the determination of the poisons treated in this Paper, he will be able to determine any of the less common ones, by referring to one of the books on this subject. The most common inorganic poisons are arsenic, phosphorus, and hydrocyanic acid, or a cyanide.

ARSENIC.

85. Preliminary Examination.—Arsenic is the most frequently used of the poisons, and generally in the form of arsenious oxide (white arsenic), which is very dangerous, as small doses are fatal, and it is almost tasteless, so that its presence cannot be detected in this way. The sample for analysis may be almost any ordinary substance—a food, vomit, or even a stomach. In case wilful poisoning is suspected, it is desirable to learn, if possible, in what form the arsenic was administered.

1. If food, vomit, or some similar substance is submitted for analysis, mix it well, set aside from one-third to one-half for further examination, or to confirm the results obtained, and mix the rest in a rather large, perfectly clean porcelain dish, with two or three times its volume of water. Stir well with a glass rod, allow the heavy solid matter to settle, and pour the liquid, together with the light suspended matter, into a second porcelain dish. Stir the solid matter with a glass rod, and feel over the bottom of the dish with the rod

for any gritty particles of solid matter. Pour the liquid from the second dish back into the first, stir well, allow it to settle, and again pour the liquid into the second porcelain dish. To the solid matter in the first dish add an equal volume of water, stir well, allow it to stand a moment for any heavy grains of solid matter to settle, pour the rest of the contents of the dish, as completely as possible without disturbing such grains, into the second dish, and examine the bottom of the dish that has just been emptied, for white grains of arsenious oxide, or black grains or scales of metallic arsenic.

If such grains are found, remove a few of them, and dry them between folds of filter paper. If black grains are found, introduce them into a closed tube and heat over the Bunsen burner, when a black mirror on the cool part of the tube shows the presence of metallic arsenic. If white grains are found, introduce them into a closed tube that is drawn out to a point, as shown in Fig. 5, so that they fall to the point *a*, and drop in a splinter of freshly ignited charcoal, which will be held at the point *b*. Now heat the charcoal to redness, and then change the position of the tube so that the white grains are heated at the same time, when, if arsenious oxide is present, a black mirror will be formed at *c*.

FIG. 5.

Whether such grains are found or not, wash the contents of the first dish into the second, and treat as directed in Art. **86.**

2. If a stomach is to be analyzed, empty the contents into a porcelain dish, turn the stomach inside out, and search the lining for white or black grains or scales, which are often found adhering to, or embedded in, the membrane, and are frequently indicated by red spots. If such grains are found, examine them for arsenic and arsenious oxide, as just described. Then cut the stomach into small pieces, mix it thoroughly with the contents in the dish, and proceed as directed in examination No. 1.

86. Method for the Determination of Arsenic in Any Form.—The reaction of the mixture in the porcelain dish is next ascertained by means of litmus paper, and, if acid, just enough pure sodium carbonate is added to render it neutral, and the whole is evaporated to a pasty consistence over the water bath. If the sample contained alcohol, the evaporation must be continued until this is completely driven off. A quantity of hydrochloric acid, of about 1.12 Sp. Gr., about equal in weight to the amount of solid substance taken for analysis, is added, together with distilled water, if necessary, in order that the hydrochloric acid shall not exceed one-third of the total liquid present. Add about 2 grams of potassium chlorate, and heat the mixture on the water bath. When the liquid has attained the temperature of the water bath, add more potassium chlorate at intervals of 5 or 10 minutes, in portions of ½ gram to 2 grams, and stir it well. Replace the water that has evaporated from time to time. Continue this treatment until the contents of the dish have become nearly homogeneous and fluid, and have assumed a light-yellow color that is retained when the substance is heated for 20 or 30 minutes longer, without the further addition of potassium chlorate.

When this point is reached, add about 1 gram of potassium chlorate, stir, and immediately remove the dish from the water bath. When the dish and contents have become perfectly cold, filter, and wash the residue well with hot water. The residue may contain metallic mercury, albuminate of mercury, lead sulphate, and possibly lead chloride, basic bismuth chloride, and stannic oxide. It should be marked Ppt. 1, and set aside to be examined for these metals, as described in Art. **87.** The filtrate and washings are usually kept separate. Heat the filtrate on the water bath, with the renewal of the water as it evaporates, until the odor given off by the chlorate has disappeared. Evaporate the washings on the water bath to about 100 cubic centimeters, and add this to the filtrate, which has been evaporated so that the total amount of liquid is from three to four times the volume of the hydrochloric acid added. Transfer the liquid to a

flask, heat it to about 70° on the water bath, and while at this temperature, conduct a slow stream of hydrogen sulphide through it for about 12 hours. Then remove the flask from the water bath, and allow the mixture to cool while the gas is still passing through it. When the contents of the flask have become cool, withdraw the delivery tube from the flask, and wash it with ammonia, allowing the washings to run into a beaker. Acidulate the ammoniacal washings with hydrochloric acid, and add this to the contents of the flask. Cover the flask loosely with filter paper, and stand it in a moderately warm place for from 6 to 12 hours. Collect the precipitate on a small filter, and wash thoroughly with water containing a little hydrogen sulphide. Saturate the filtrate and washings with hydrogen sulphide, and evaporate to a small bulk over the water bath. If any precipitate is formed during the evaporation, filter it off, wash well, and add it to the main precipitate. The filtrate should be examined for the metals of the third, fourth, and fifth groups. The precipitate contains the arsenic, together with any other metals of the first and second groups that may be present, and generally some organic matter. Remove the precipitate and filter to a small porcelain dish, and heat it on the water bath until perfectly dry. Add pure fuming nitric acid (which must be free from chlorine), drop by drop, until the precipitate is thoroughly moistened, and again evaporate to dryness on the water bath. Moisten the precipitate with pure concentrate sulphuric acid, heat for about 2 hours on the water bath, and then on the sand bath at a moderate temperature, gradually raising the temperature until white fumes begin to escape. The mass should now be easily broken up, and a small portion of it when stirred with a little water should not impart any considerable color to the fluid. If it gives a brown color to the water, or if the mass should have a brown, oily appearance, add some small pieces of pure dry filter paper, and heat the mass till white fumes again begin to come off, and then allow the dish and contents to become nearly cold. Add a mixture of 1 part of concentrate hydrochloric acid and 8 parts of water, and heat on the water bath

for about 1 hour, stirring occasionally. Filter, wash well with hot water containing a little hydrochloric acid, and finally with boiling water. The undissolved portion on the filter, which may contain lead, mercury, tin, bismuth, and antimony, should be marked Ppt. 2, and set aside for examination according to Art. **87.**

The filtrate is removed to a flask, and hydrogen sulphide again conducted through it, exactly as described in the first precipitation, by hydrogen sulphide. The precipitate, which is now free from organic matter, is collected on a small filter and washed. It will contain all the arsenic, and perhaps some other metals as sulphides. If the precipitate is yellow, and a small portion of it, when shaken in a test tube with ammonium carbonate, completely dissolves, arsenic alone is present. In this case, dissolve it in ammonia, evaporate the solution to dryness on the water bath, add a little fuming nitric acid, heat, then add concentrate sulphuric acid, and evaporate on the sand bath until all nitric acid is expelled, and white fumes begin to come off. Allow the residue to cool, add from 5 to 10 cubic centimeters of sulphurous acid, evaporate the excess on the water bath, and examine the resulting solution for arsenic by one of the methods to be given later.

If the precipitate contains other metals than arsenic, remove the filter, together with the precipitate, to a small porcelain dish, pour ammonia over the precipitate, add a few drops of ammonium sulphide, and remove the filter, washing it thoroughly with as little water as possible. Heat the dish and contents on the water bath while stirring the mixture. Filter, wash, and mark the residue Ppt. 3, to be examined according to Art. **87.** Evaporate the filtrate to dryness on the water bath, add a little pure fuming nitric acid, and again evaporate until nearly dry. To the residue add a little sodium hydrate, and then sodium-carbonate solution in slight excess. Now add a mixture of 1 part of sodium carbonate and 2 parts of sodium nitrate; evaporate to dryness over the water bath, remove to a Bunsen flame, and gradually increase the heat until the substance fuses. Allow the fusion to cool, add cold water, and stir frequently until the

mass is thoroughly disintegrated, when all the arsenic will be dissolved. If a residue remains undissolved, filter it off, wash, and examine it for antimony and tin. To the filtrate add pure dilute sulphuric acid until the reaction is strongly acid, evaporate nearly to dryness on the water bath, add a little more dilute sulphuric acid, and heat on the sand bath until heavy white fumes begin to come off. Cool the residue, add from 5 to 10 cubic centimeters of sulphurous acid, and heat on the water bath till most of the excess of sulphurous acid is driven off. Add a little water to make a clear solution, and test for arsenic by one of the following methods:

1. *Marsh's Test.*—This test is applied in exactly the same manner as described in Art. **72.** The solution prepared as directed above is added in the same way as the water is added, and the black mirror or stain shows the presence of arsenic. Only a little of the arsenic solution should be added at a time, for, if much is added, it may cause violent action, which would interfere with the test, or perhaps cause its loss, through foaming over. In many cases a solution of arsenic may be tested directly by this method, without the long preparation above described, but when absolutely accurate results are desired, and organic matter is present, the above directions should be carefully followed.

2. *Fresenius' and von Babo's Method.*—Add a little water to the solution obtained as described above, transfer it to a small flask, heat to 70°, and precipitate the arsenic by a current of hydrogen sulphide, as previously directed, except that in this case all the arsenic will be precipitated in 6 hours. Filter, wash well, and, if much is present, dry the filter and precipitate, remove the thoroughly dry precipitate to a porcelain boat, and proceed directly with its reduction. If the precipitate is too small to be removed from the filter, dissolve it while wet with a little ammonia; allow the solution to run into a porcelain crucible, add from $\frac{1}{5}$ to $\frac{1}{2}$ gram of dry sodium carbonate, evaporate to dryness on the water bath, and remove the dry residue, or the precipitate as obtained above, to a porcelain boat *c*, Fig. 6, mix it with about twice its weight of pure potassium cyanide and 5 or

6 times its weight of pure dry sodium carbonate, and place the boat and contents in a hard-glass tube, drawn out at one end. Connect the apparatus as shown in Fig. 6, and after the tube is thoroughly filled with carbon dioxide—generated by the action of hydrochloric acid on marble, in the Kipp apparatus *a*, and washed by concentrate sulphuric acid in the

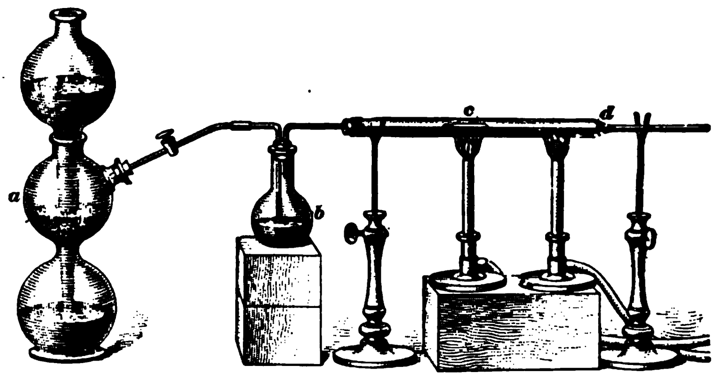

FIG. 6.

flask *b*—gently heat the tube throughout its entire length, to be sure all moisture is driven off. Then regulate the flow of carbon dioxide so that it passes through the flask *b* at the rate of about one bubble per second, gradually heat the tube to redness near the point *d*, where it begins to narrow, then place a second burner under the boat at *c*, gradually increasing the heat until the tube is bright red and the contents of the boat are thoroughly fused, continuing the heat until all the arsenic is driven off. The arsenic will be deposited on the tube just beyond the burner at the point *d*, and in the narrow part of the tube, forming a metallic mirror. If any arsenic is not deposited on the tube, but escapes, it may be detected by its garlic odor. In this determination the carbon dioxide should always be generated in Kipp's, or some similar generator, so that its flow may be properly regulated.

87. Examination of the Residues or Precipitates. Although the main object of this process is the determination of arsenic, the insoluble residues obtained while carrying it

out should be examined for other poisonous metals. This may be done as follows:

1. *Examination of Ppt. 1.*—This residue may contain lead, mercury, bismuth, and tin. When dry, remove it to a porcelain dish, add red fuming nitric acid, and evaporate almost to dryness on the water bath. Add water and a little common nitric acid, and continue the heating for some time; then filter, dilute the filtrate, precipitate with a current of hydrogen sulphide, and examine the precipitate for the metals mentioned above, as directed under the group separations in *Qualitative Analysis*, Part 1. The precipitate may contain a little lead, and should be examined for it.

2. *Examination of Ppt. 2.*—This residue may contain lead, mercury, antimony, and possibly tin and bismuth. Remove it to a small porcelain dish, add an excess of aqua regia, heat for some time on the water bath, and finally boil down to a small bulk on the sand bath or over the flame. Add water and a little hydrochloric acid, bring the solution to boiling, and if an insoluble residue remains, filter it off. Precipitate the metals from the filtrate by a current of hydrogen sulphide, and examine the precipitate as directed under the group separations in *Qualitative Analysis*, Part 1.

3. *Examination of Ppt. 3.*—This residue may contain lead, mercury, and possibly copper. Remove it to a porcelain dish, and heat on the water bath with a mixture of equal parts of concentrate and dilute nitric acid, for half an hour, and then bring to boiling on the sand bath or over the flame. Mercury will not be attacked by this acid, but other metals that may be present will be dissolved. Dilute, filter, and examine the precipitate and filtrate, as directed under the separation of the metals of the second group in *Qualitative Analysis*, Part 1.

PHOSPHORUS.

88. Preliminary Examination for Phosphorus.—Phosphorus has been quite largely used in poisoning mice, etc., and its poisonous properties have become quite

generally known. Consequently, the chemist is occasionally called upon to examine the contents of a stomach, an article of food, or some similar substance, for phosphorus. In such cases the chemist should direct his attention exclusively to the detection of phosphorus in the free state. Merely finding phosphoric acid would not prove anything, for this is a constituent of nearly all animal and vegetable bodies. In examining a substance for phosphorus, there should be no unnecessary delay, for in the air the phosphorus is oxidized to phosphorous acid, and finally to phosphoric acid.

The first step in the examination of a substance for unoxidized phosphorus is to ascertain if its presence is indicated by the odor of the substance, or by phosphorescence when the sample is stirred in a perfectly dark room. These tests furnish strong indications, but cannot be depended on, as the odor and phosphorescence may both be due to other substances. Next, place a little of the sample in a small flask, and, if dry, moisten it with water. In the mouth of the flask, loosely fit a cork to which is fastened a strip of filter paper saturated with a neutral solution of silver nitrate, and heat the flask and contents to about 40°. If the paper is not colored after an hour of this treatment, it is scarcely possible that free phosphorus is present, and it is hardly necessary to proceed further with the examination, but the result may be confirmed by one of the following methods. If the paper is blackened, phosphorus is indicated but not proved, as the blackening may be caused by other substances. Consequently, in this case, the substance must be further examined by one of the following methods.

89. Examination by Means of Distillation With Water.—Mix a rather large portion of the sample with water and a little dilute sulphuric acid in the flask *a*, Fig. 7, and connect it with a Liebig condenser *b c*. Place a screen *e f* of some opaque material between the flask and the condenser to prevent the light of the lamp falling upon the condenser, and distil the contents of the flask, receiving the distillate in a flask *d*. This experiment must be performed

in a dark room. If the substance contains free phosphorus, there will be seen a strong luminous ring that usually moves up and down near the point *b* where the steam enters the cooled part of the tube. Samples that contain only very small quantities of phosphorus usually produce a luminous ring that may be seen continuously for half an hour. If much phosphorus is present, it will collect in small globules in the bottom of the flask *d* and may be further examined. If phosphorus has been introduced into the substance in the form of phosphorus matches, an oxidizing agent will always be present. In this case a little ferrous sulphate should be added with the sulphuric acid, in order to destroy the oxidizing agent; and if hydrogen sulphide is present, a little ferric chloride should also be added. Ether, alcohol, oil of turpentine, and many other ethereal oils prevent the luminosity so long as they are present. Ether and alcohol are soon distilled over, and the luminosity will then appear, but many of the ethereal oils prevent it permanently, and when they are present the method described in Art. **90** should be employed.

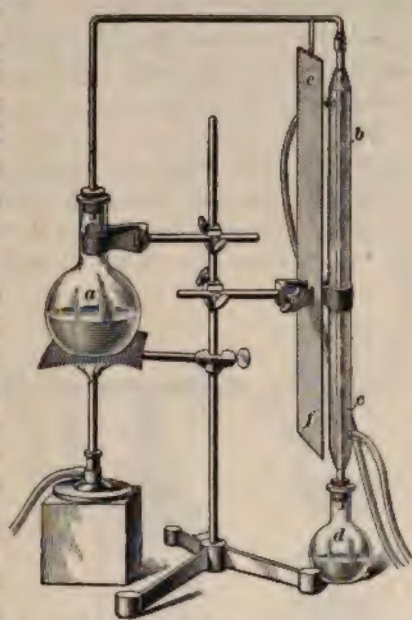

FIG. 7.

Instead of the apparatus shown in Fig. 7, the ordinary form of distilling apparatus shown in Fig. 25, *Theoretical Chemistry*, may be used; but the form shown in Fig. 7 is better for this purpose.

90. Examination by Driving Off Phosphorus in a Current of Carbon Dioxide.—The method just described

in Art. 89 is easily carried out, and yields conclusive results even with minute quantities of phosphorus, when substances that prevent the reaction are absent. But as a number of substances prevent the formation of a luminous ring, whenever this reaction fails a portion of the sample should be treated as follows:

Place the substance in a flask, add water, and then dilute sulphuric acid until the reaction of the liquid is distinctly acid. Fit the flask *d*, Fig. 8, with a stopper having two perforations, through one of which a glass tube *c* passes nearly to the bottom of the flask; and through this tube pass a

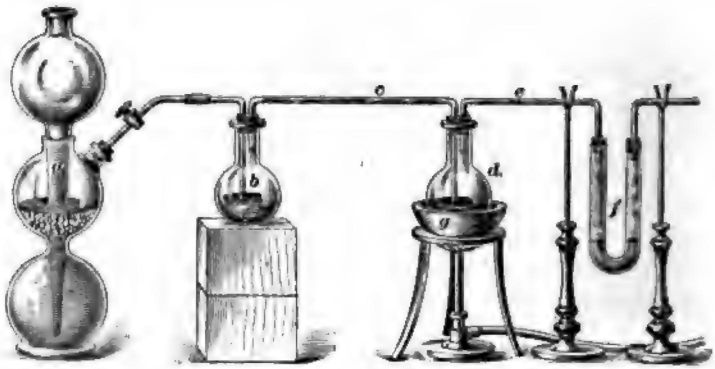

FIG. 8.

slow current of carbon dioxide, which has been generated in the Kipp apparatus *a*, and washed in the flask *b* containing concentrate sulphuric acid. Connect the tube *e*, which passes through the other perforation, and through which the gas passes from the flask *d*, with a **U** tube *f* containing a neutral solution of silver nitrate, so that the gas passes through this solution. When the flask *d* is thoroughly filled with carbon dioxide, place it on the water bath *g*, and, while heated on the bath, pass a slow current of carbon dioxide through it for several hours. If the substance contains phosphorus, it will be carried over unoxidized, by the carbon dioxide, and form a black precipitate of silver phosphide and metallic silver, when it comes in contact with the silver-nitrate solution. If no precipitate is formed in the **U** tube

after several hours, free phosphorus is not present, and the operation need not be carried further. If a black precipitate is formed, it is an indication of phosphorus, but is not conclusive, as it may be formed by other substances, and must be further examined. In this case, filter the contents of the tube, wash the precipitate well with water, and proceed as follows:

Place some zinc in the two-necked Woulff bottle *a*, Fig. 9, and add dilute sulphuric acid through the funnel tube *b*,

FIG. 9.

which must be large enough to hold more than the total amount of acid added. Lead the hydrogen thus generated through the **U** tube *c*, which contains pumice stone saturated with a concentrate solution of potassium hydrate, to absorb any hydrogen sulphide that may be present. Connect the tube leading from the **U** tube with a tube having a platinum tip at *e*, by means of a piece of rubber tubing over which a screw pinch cock *d* is fitted, and by means of this pinch cock regulate the flow of hydrogen so that it will burn at *e* with a steady flame. If this flame is colorless, and does not produce a green coloration when allowed to impinge on a piece of cold porcelain, the gas is free from hydrogen phosphide. Now wash the precipitate, supposed to contain

silver phosphide, into the generator a, through the funnel tube b. If this precipitate contains phosphorus, hydrogen phosphide will be formed in the generator, and in a few moments the inner cone of the flame will become green, and an emerald-green coloration will be imparted to the cold porcelain.

HYDROCYANIC ACID.

91. Preliminary Examination.—If an article of food, the contents of a stomach, or some other substance is to be examined for hydrocyanic acid or a cyanide—most frequently potassium cyanide—which has the same effect as the acid, there should be as little delay as possible, as hydrocyanic acid is quite readily decomposed and may be lost, and it has been claimed, but not thoroughly demonstrated, that hydrocyanic acid is formed during the decomposition of animal matter. If the sample for examination does not have an odor of its own, the presence of hydrocyanic acid will be revealed by its well known odor; but, if the substance with which it is mixed has a strong odor, that of the hydrocyanic acid may be completely hidden. In any event, the odor alone cannot be depended on, as nitrobenzol and benzaldehyde have odors somewhat similar to that of hydrocyanic acid.

Mix a small portion of the sample with water, filter, and test part of the filtrate with ferric chloride for ferrocyanides and sulphocyanides, and the other part with ferrous sulphate for ferricyanides. Then proceed with the examination according to the information obtained by these tests.

92. Examination for Hydrocyanic Acid When Ferrocyanides, Ferricyanides, and Sulphocyanides Are Absent.—If the preliminary examination has shown that ferrocyanogen, ferricyanogen, and sulphocyanogen compounds are absent, mix the substance with water, add a solution of tartaric acid until the substance has a strong acid reaction, and introduce it into the retort a, Fig. 10, through the tubulure b. Tightly stopper the tubulure, and lower the retort into a vessel c containing a solution of calcium

chloride, so that it does not touch the bottom of the vessel. Slant the neck of the retort upwards, and heat the calcium-chloride bath until the contents of the retort begin to boil. Lead the vapors through a Liebig condenser, the lower end of which is connected with a tube that passes through one of the perforations of a doubly perforated stopper that is closely fitted into the top of the cylinder *d*. Through the other perforation of this stopper pass a tube that leads to the **U** tube *e*, containing a dilute solution of pure sodium hydrate, to

FIG. 10.

absorb any hydrocyanic acid that may pass over. When about 10 cubic centimeters of distillate have collected in the cylinder *d*, replace it with another cylinder, divide the distillate into three parts, and test them as follows:

1. To one-third of the distillate in a test tube, add a little ferrous-sulphate solution, a drop of ferric-chloride solution, and then enough sodium hydrate to give the liquid an alkaline reaction, when, if hydrocyanic acid is present, a greenish-blue precipitate will be formed that consists of a mixture of ferric ferrocyanide and the hydrates of iron. Now add hydrochloric acid, which will dissolve the hydrates of iron, and leave a blue precipitate of ferric ferrocyanide, or, if only

a minute quantity of hydrocyanic acid is present, a greenish solution will be left in the tube, from which a slight blue precipitate will settle upon standing.

2. Place a second portion of the distillate in a porcelain dish, add a drop of sodium-hydrate solution, then sufficient yellow ammonium sulphide to impart a yellowish color to the solution, and slowly evaporate to dryness on the water bath. If the solution contained hydrocyanic acid or a cyanide, the residue in the dish will contain sodium sulphocyanide. Dissolve this residue in a little water, add 4 or 5 drops of hydrochloric acid, allow it to stand a few minutes, and then add a few drops of ferric chloride. A red coloration shows the presence of a sulphocyanide that has been formed from hydrocyanic acid by the above treatment. In case the red color is not permanent, or a violet color is formed, more of the ferric chloride must be added to produce a permanent red color.

3. To the third portion of the filtrate, add a few drops of potassium-nitrite solution, about 3 drops of ferric chloride, and then just enough dilute sulphuric acid to change the color of the ferric salt formed from brown to light yellow. Heat the solution carefully, until it just commences to boil, and, after allowing it to cool, add ammonia in slight excess, to precipitate the excess of iron. Filter off the precipitate, and to the filtrate, which should still contain free ammonia, add a few drops of hydrogen sulphide. If the solution contained hydrocyanic acid, potassium nitroprusside will be formed, and the hydrogen sulphide acting upon this imparts a violet color to the solution.

The second filtrate that collects in the cylinder should be tested in the same manner, and finally the contents of the U tube should be subjected to the same tests.

93. Determination of Hydrocyanic Acid When Ferrocyanides, Ferricyanides, or Sulphocyanides Are Present.—If the preliminary examination has shown the presence of ferrocyanogen, ferricyanogen, or sulphocyanogen compounds, mix the sample with water, add a little tartaric

acid, and then sodium carbonate until the sample is slightly alkaline. Introduce the sample into a retort, and heat over the water bath to about (but not exceeding) 60°, while leading a slow current of washed carbon dioxide through the tubulure, nearly to the bottom of the retort. The carbon dioxide should be generated in a Kipp apparatus, and washed in concentrate sulphuric acid. Collect the distillate in a cylinder to which a **U** tube containing sodium hydrate is attached, as shown in Fig. 10, and subject the distillate to the tests described in Art. **92**.

THE ALKALOIDS.

94. The detection and separation of the alkaloids is much more difficult than the detection and separation of the metals. This is due to several causes. Reagents do not give the same sharp distinction between the alkaloids that is seen in the case of the metals, and, as the alkaloids form a comparatively new field of chemistry, and have not been thoroughly studied, in many cases the reactions are not understood, and only the outward appearance known, so that the conditions that may modify these reactions are not known.

As new alkaloids, of whose reaction nothing is known, are continually being discovered, anything like a complete treatment of this subject is impossible at the present time. Only a few of the most common alkaloids, therefore, will be treated in this course. This will be sufficient for the average student, but if a student wishes to know more of this subject, after making himself familiar with the alkaloids treated in this Paper, he will be in a position to widen his range of knowledge in this field, by reading and investigation.

VOLATILE ALKALOIDS.

95. The volatile alkaloids are liquids at ordinary temperatures. They may be volatilized either in the pure state or when mixed with water, and, consequently, are obtained

in the distillate when their salts are distilled with strong fixed bases and water. When their vapors come in contact with the vapor of a volatile acid, they form a white cloud, similar to that formed by ammonia and hydrochloric acid. The most common volatile alkaloids are *nicotine* and *conine*. They are most easily detected when in the pure state, and, consequently, should be obtained as nearly as possible in that condition before applying tests for them. To do this, add sodium-hydrate solution to the aqueous solution of the alkaloids, and distil them in a current of hydrogen, which has been generated in a Kipp apparatus, and lead into the retort containing the solution. Neutralize the distillate with oxalic acid, and evaporate slowly. Dissolve the oxalate of the alkaloid in alcohol, filter off any residue that may be present, and evaporate the solution. Treat the residue with water, add sodium-hydrate solution, shake this mixture with ether, separate the ethereal solution, and allow the ether to evaporate at about 20°, leaving the pure alkaloid.

96. Nicotine.—Nicotine in the pure state is a colorless, oily liquid, with a disagreeable odor. It is found in the tobacco plant, especially in the leaves and seeds. When allowed to stand in the air, it assumes a yellowish or brownish color. When heated to boiling (247°) in the air, it partially decomposes, but may be distilled in an atmosphere of hydrogen without decomposition. It mixes with water in all proportions, and dissolves easily in alcohol or ether.

Nicotine has a pungent taste, and is very poisonous. It acts as a moderately strong base, precipitating metals as hydrates, and forming salts with acids. Most of these salts are non-volatile, and easily soluble in water or alcohol, but insoluble in ether. They are odorless, but have a strong taste of tobacco.

1. A solution of nicotine in water, or a nicotine salt mixed with sodium hydrate, when shaken with ether, forms a solution of nicotine in ether. If this ethereal solution is removed to a watch glass, and the ether evaporated at a temperature of about 20°, the nicotine will remain on the

ıtch glass in drops or streaks. If this is now heated, the :otine will be volatilized, forming white fumes, with a ·ong, disagreeable odor.

2. *Platinum chloride*, when added to a rather strong .ution of nicotine or one of its salts, produces a light-llow, flocculent precipitate that dissolves upon heating; t, if the heat is continued, an orange-yellow crystalline ecipitate soon separates from this solution. If the solution rather weak and contains free hydrochloric acid, the pre-)itate may not form for some time, and from a rather ·ong solution in alcohol, containing a little free hydro-loric acid, a yellow precipitate forms at once.

3. *Gold chloride*, when added to a solution of nicotine or ;e of its salts, in water, forms a reddish-yellow precipitate at is slightly soluble in hydrochloric acid.

4. *Iodine solution*,* when added in small quantity to a lution of nicotine in water, produces a yellow precipitate at, upon standing, dissolves in the solution. If a little ore of the iodine solution is added to this solution, a bright ddish-brown precipitate is formed that also disappears)on standing. If iodine solution is added to a solution of nicotine salt, the reddish-brown precipitate is formed at ıce.

5. *Picric acid*, when added in excess to a solution of cotine in water, or to a neutral solution of a nicotine salt, :oduces a yellow precipitate that is soluble in hydrochloric :id.

6. *Tannic acid*, added to an aqueous solution of nicotine, :oduces a white precipitate that is soluble in hydrochloric ' sulphuric acid.

7. *Silver nitrate*, when added to a solution of nicotine in ater or alcohol, slowly imparts a brown color to the solu-)n, and finally a black precipitate separates.

8. *Concentrate sulphuric acid*, or *nitric acid* of 1.2 Sp. Gr., ssolves nicotine in the cold to a colorless solution, but tric acid of 1.3 Sp. Gr. forms a red solution.

* To make this solution, dissolve about 20 grams of potassium iodide water, add 13 grams of iodine, stir, and dilute to 1 liter.

9. When a drop of nicotine is gently warmed with 4 or 5 drops of hydrochloric acid of 1.12 Sp. Gr., it forms a brown solution. If to this a drop of nitric acid of 1.4 Sp. Gr. is added, after the solution has become cool, it gives the solution a reddish-violet color that gradually changes to red.

10. If a few drops of a solution of nicotine in water, or of a neutral solution of nicotine hydrochloride, are added to an excess of mercuric-chloride solution, a white, flocculent precipitate is produced that is soluble in ammonium chloride or hydrochloric acid.

97. Conine.—Conine is a colorless, oily liquid that becomes brown when exposed to the air. It occurs in the spotted hemlock, especially in the green seed. When heated in the air to the boiling point (about 168°), it partly decomposes and becomes brown, but may be distilled unaltered in an atmosphere of hydrogen. It is only slightly soluble in water, but dissolves readily in alcohol or ether, and its solutions have a strong alkaline reaction. Conine is a strong base. It slowly volatilizes at ordinary temperatures, giving off poisonous vapors with a pungent, stupefying odor, which give dense white fumes with the vapor of a volatile acid. It precipitates metals as hydrates in a manner similar to ammonia, and with the acids it forms salts that are soluble in water or alcohol, but are insoluble, or nearly so, in ether.

1. When an aqueous solution of a conine salt is mixed with sodium hydrate, and this mixture is shaken with ether, the conine dissolves in the ether. If this ethereal solution is now evaporated on a watch glass at about 25°, the conine will remain on the watch glass in yellowish, oily drops.

2. *Platinum chloride* does not produce a precipitate in solutions of conine salts, even when concentrate.

3. *Gold chloride*, when added to a rather strong solution of conine hydrochloride, produces a light, yellowish precipitate that is insoluble in hydrochloric acid.

4. *Iodine solution* acts in the same way with a conine solution that it does with nicotine.

5. *Picric acid*, in concentrate solution, when added to

conine that is covered with a little water, produces a yellow precipitate; but, if the solution is at all dilute, no precipitate is formed.

6. *Silver nitrate*, when added to a solution of conine in alcohol, yields a grayish-brown precipitate at once.

7. *Mercuric chloride*, when added in excess to a conine solution, produces a white precipitate that is soluble in hydrochloric acid.

8. *Chlorine water*, when added to conine that is covered with a little water, produces a white precipitate that dissolves easily in hydrochloric acid.

9. *Concentrate sulphuric acid*, or *nitric acid* of 1.4 Sp.Gr., dissolves conine in the cold without coloration.

NON-VOLATILE ALKALOIDS.

Solid alkaloids that cannot be distilled with water.

GROUP I.

Non-volatile alkaloids that are precipitated from solutions of their salts by sodium hydrate, and dissolve in an excess of the reagent.

Morphine *Cocaine*

98. Morphine.—Morphine is a white crystalline substance obtained from opium, the dried juice of the seed capsules of the poppy. It is very slightly soluble in cold water, but dissolves somewhat more freely in hot water; it dissolves somewhat more readily in alcohol, but is most readily dissolved by amyl alcohol, especially when hot. Its solutions have a bitter taste and an alkaline reaction. It unites with acids, neutralizing them and forming salts that are easily soluble in water and most of them also in alcohol. Morphine and its salts are poisonous.

1. *Sodium hydrate* or ammonia precipitates morphine from solutions of its salts, in the form of a white crystalline powder. Shaking promotes the formation of this precipitate, which is generally slow in separating. It dissolves very readily in an excess of sodium hydrate, less easily in

ammonia, and with difficulty in ammonium carbonate. If the solution in sodium hydrate is shaken with ether, but very little of the morphine will be taken up; it is all dissolved, however, when shaken with warm amyl alcohol.

2. *Sodium carbonate* precipitates morphine as a white powder that is insoluble in an excess of the reagent. Consequently, if carbon dioxide is led into the solution of morphine in sodium hydrate, it will precipitate the morphine by changing the sodium hydrate to carbonate.

3. *Sodium bicarbonate* precipitates morphine, in the form of a white powder, from neutral solutions of its salts, but does not form a precipitate in acid solutions.

4. *Picric acid*, when added to a concentrate neutral solution of a morphine salt, produces a yellow precipitate that dissolves quite readily in water. Hence, no precipitate is formed in neutral solutions.

5. *Tannic acid*, when added to an aqueous solution of a morphine salt, produces a white precipitate that dissolves readily in acids.

6. *Concentrate nitric acid*, when added to morphine or one of its salts, in the dry state or in concentrate solution, produces a reddish-yellow color that is not changed by the addition of stannous chloride. Nitric acid does not impart a color to dilute solutions in the cold, but if heated, they assume a yellowish color.

7. If morphine is dissolved in pure, concentrate sulphuric acid in the cold, and a small fragment of potassium nitrate is added, a brown coloration is produced at the point of contact. Sometimes the color is reddish at first, but rapidly changes to brown. If the sulphuric-acid solution of the morphine is allowed to stand for 15 hours in the cold, or is heated for half an hour at 100°, before adding the potassium nitrate, and is then cooled and a small piece of potassium nitrate added, it imparts a blood-red color to the solution. Sometimes the potassium nitrate gives the solution a violet color at first, but this rapidly changes to red.

8. If a little morphine is dissolved in concentrate sulphuric acid, a little sodium arsenate added, and the solution

heated, it assumes a reddish-brown color. If this solution is cooled, and water is slowly added, the color changes first to red and then to green. If this green solution is shaken with ether, it gives the ethereal solution a reddish-violet color. If shaken with chloroform, a deep-violet color is produced.

9. If a small quantity of morphine is dissolved in about 1 cubic centimeter of concentrate hydrochloric acid, a drop of concentrate sulphuric acid added, and the solution is placed on a watch glass and evaporated over the water bath, a purple residue remains on the glass. If, to this residue, a few drops of hydrochloric acid are added, and then enough saturated solution of sodium bicarbonate to render it neutral or slightly alkaline, a drop or two of a solution of iodine in alcohol will impart a green color to the solution. Ether, when shaken with this solution, dissolves the coloring matter, forming a layer of solution with a reddish-violet color.

10. A simple test for morphine may be made by mixing a little of the morphine with about six times its weight of white sugar, and adding a few drops of concentrate sulphuric acid to this mixture. The solution thus obtained will have a red color that changes to green, and finally to brownish yellow. If a morphine solution is to be tested, to a small portion add as much white sugar as it will dissolve, and then a few drops of concentrate sulphuric acid. The addition of a drop or two of bromine water is said to increase the delicacy of this reaction.

11. If a small fragment of morphine or a morphine salt is added to a small quantity of a solution, containing about 1 gram of ammonium molybdate in 10 cubic centimeters of concentrate sulphuric acid, in a porcelain dish, and broken up with a stirring rod, it gives the solution a violet color that gradually changes to green, while the edge of the solution appears blue. If this is now stirred, the color changes to a brownish green, and finally to deep blue. If a drop of rather dilute solution of a morphine salt is added to the molybdate solution, a blue ring is formed that gradually extends to the whole of the solution. The solution of ammonium molybdate in sulphuric acid must be freshly prepared, as it rapidly decomposes.

99. Cocaine.—Cocaine is a white crystalline substance obtained from coca leaves. It has a bitter taste, and possesses the property of destroying the sense of feeling. It dissolves slightly in water, more easily in alcohol, and still more readily in ether. Its solutions have an alkaline reaction. It dissolves readily in acids, forming salts, most of which are soluble in water and alcohol, but insoluble, or nearly so, in ether.

1. *Sodium hydrate*, when added to a solution of a cocaine salt, produces a white precipitate that is slightly soluble in an excess of the reagent.

2. *Ammonium hydrate* gives a reaction similar to sodium hydrate, but the precipitate dissolves much more readily in an excess of the ammonia. If a little ether is shaken with the solution in ammonia, it takes up the cocaine, which will be deposited in needles when this ethereal solution is evaporated in the air.

3. *Sodium carbonate*, added to a solution of a cocaine salt, produces a white precipitate that is insoluble in an excess of the reagent.

4. *Tannic acid*, added to a solution of cocaine that contains hydrochloric acid, produces a yellow precipitate that forms a resinous mass when shaken, or upon standing.

5. *Mercuric chloride*, when mixed with a solution of a cocaine salt, produces a white precipitate that is soluble in hydrochloric acid, ammonium chloride, or alcohol.

6. *Stannous chloride*, when added to a concentrate solution of a cocaine salt, produces a curdy, white precipitate that is soluble in nitric acid.

7. *Concentrate sulphuric acid* dissolves cocaine to a colorless solution that is not colored by nitric acid or nitrates. Molybdic acid and white sugar also fail to produce characteristic colors.

8. *Nitric acid* of 1.4 Sp. Gr. dissolves cocaine or its salts to a colorless solution. If this solution is evaporated on the water bath, and a few drops of a solution of potassium hydrate in alcohol are added to the residue, the whole being stirred, a characteristic odor, similar to that of peppermint, is given off.

9. *Potassium chromate*, when added to a rather strong solution of cocaine that contains a very little free hydrochloric acid, precipitates yellow cocaine chromate, which is soluble in an excess of hydrochloric acid, or in a large quantity of water.

10. If a little cocaine is dissolved in about 1 cubic centimeter of concentrate sulphuric acid, a quantity of potassium iodate, amounting to about three times the weight of the cocaine, is added, and the whole is heated on the water bath; it first assumes a yellow color, then green streaks appear that grow darker, and gradually spread to the whole of the liquid, and finally the whole solution becomes brown.

11. If cocaine and concentrate hydrochloric acid are sealed in a strong glass tube, and heated on the water bath for 3 or 4 hours, the cocaine will be decomposed, and methyl alcohol and benzoic acid will be formed. If considerable cocaine was present, white crystals of benzoic acid will separate when the tube is allowed to cool.

12. If a little cocaine solution is added to 2 or 3 cubic centimeters of chlorine water, and to this a few drops of palladium chloride are added, a red precipitate is formed.

100. Separation of Morphine and Cocaine.—Cocaine may be separated from morphine by rendering a solution of their salts just alkaline with ammonia, and shaking with petroleum ether. This extracts the cocaine, but does not dissolve the morphine. The cocaine is obtained by evaporating the petroleum-ether solution.

GROUP II.

Non-volatile alkaloids that are precipitated by sodium hydrate, and are insoluble in an excess of the reagent, and are also precipitated by sodium bicarbonate, even from acid solutions.

Quinine *Cinchonine* *Narcotine*

101. Quinine.—Quinine is a white crystalline substance found in cinchona bark. It is slightly soluble in water, but dissolves more readily in alcohol or ether. It is exceedingly

bitter, and its solutions are alkaline. It unites with acids, forming neutral and acid salts. The neutral salts are sparingly soluble in cold water, but more readily soluble in hot water or alcohol, while the acid salts dissolve readily in water.

1. *Sodium hydrate* precipitates quinine from solutions of its salts, in the form of a white powder, which is insoluble in an excess of the reagent.

2. *Ammonium hydrate* produces a white precipitate that is slightly soluble in an excess of the reagent. If the mixture containing the precipitate formed by ammonia is shaken with ether, to which about 2 per cent. of alcohol is added, the precipitate is dissolved and two clear layers of liquid are formed.

3. *Sodium carbonate* precipitates quinine in the form of a white powder that is insoluble, or but slightly soluble, in an excess of the reagent.

4. *Sodium bicarbonate*, when added to a rather strong neutral or acid solution of a quinine salt, produces a white precipitate that is very slightly soluble in an excess of the reagent.

5. *Tannic acid*, when added to an aqueous solution of a quinine salt, produces a white precipitate that is soluble in a little hydrochloric acid, and is reprecipitated by the addition of more hydrochloric acid. The precipitate is also soluble in acetic acid.

6. *Concentrate sulphuric acid* dissolves quinine and its salts to a colorless or faintly-yellowish solution. If this solution is cautiously heated, it becomes yellow, and finally brown.

7. *Nitric acid* of 1.4 Sp. Gr. dissolves quinine and its salts to a colorless solution that generally has a bluish opalescence, and turns yellow when heated.

8. If, to a solution of a quinine salt, about one-sixth its volume of strong chlorine water is added, and then ammonia is added slowly until the reaction of the solution is alkaline, an emerald-green coloration is produced. This test may be varied by adding chlorine water, then potassium ferrocyanide,

and finally ammonia, when the solution will assume a deep-red color that rapidly changes to brown. The addition of acetic acid to the red solution destroys the color, but it may be restored by the careful addition of ammonia. This is a delicate and characteristic reaction, but is prevented by the presence of morphine.

9. If a drop of water is added to a small piece of potassium hydrate and this is fused, and, while still warm, a solution of quinine in alcohol is added, the alcohol evaporated off, and the residue gently heated, a green color is imparted to the mass. Other alkaloids give similar, but not the same, colors.

10. A characteristic test for quinine may be made by dissolving a little of the sulphate in acetic acid, adding a little alcohol, and then a solution of iodine in alcohol until the solution has a brownish-yellow color, when a black precipitate will separate, either at once or after standing a few minutes.

102. Cinchonine.—Cinchonine is a white crystalline substance, found in cinchona bark, together with quinine and other bases. It is almost insoluble in water, and but slightly soluble in alcohol containing water, but somewhat more readily in absolute alcohol, especially when hot. It is most readily dissolved in a mixture consisting of 3 parts of chloroform and 1 part of alcohol. Its solutions have a bitter taste and an alkaline reaction. Cinchonine neutralizes acids completely, forming salts that have a bitter taste, are soluble in water and alcohol, but insoluble, or nearly so, in ether.

1. *Sodium hydrate* precipitates cinchonine from solutions of its salts, in the form of a white powder that is insoluble in an excess of the reagent.

2. *Ammonium hydrate* gives the same reaction as sodium hydrate.

3. *Sodium carbonate*, when added to a solution of a cinchonine salt, produces a white precipitate that is insoluble in an excess of the reagent.

4. *Sodium bicarbonate* precipitates cinchonine, in the

form of a white powder, from moderately strong solutions of its salts.

5. *Tannic acid*, when added to an aqueous solution of a cinchonine salt, produces a white precipitate that dissolves in a little hydrochloric acid, and is reprecipitated if more hydrochloric acid is added. It is also soluble in acetic acid. (Compare Art. **101**, 5.)

6. *Concentrate sulphuric acid* dissolves cinchonine to a colorless solution that becomes brown, and finally black, when heated.

7. If cinchonine is dissolved in concentrate sulphuric acid, and a little concentrate nitric acid is added, the solution remains colorless in the cold; but, when heated, it first becomes yellowish, then brown, and finally black.

8. If, to a solution of a cinchonine salt, about one-fifth its volume of strong chlorine water is added, and then ammonia, until the reaction of the liquid is alkaline, a yellowish-white precipitate is formed.

9. If a little potassium hydrate is fused, with the addition of a drop of water, a little solution of cinchonine in alcohol is added, and the residue is carefully heated, after evaporating the alcohol, a reddish-brown or violet color is at first imparted to the mass, which, upon the continued application of heat, changes to bluish green, and vapors with a pungent odor are evolved.

10. *Potassium ferrocyanide*, when added to a neutral solution of a cinchonine salt, or one containing but little free acid, precipitates yellow, flocculent cinchonine ferrocyanide. If an excess of the reagent is added and the mixture is gently heated, the precipitate dissolves, but, upon cooling, it separates again in golden-yellow crystals.

103. Narcotine.—Narcotine is a white crystalline substance obtained from opium. It is almost insoluble in water, and only sparingly soluble in alcohol and ether, but dissolves readily in chloroform. Narcotine is tasteless, but its solutions are exceedingly bitter, and do not color litmus paper. It dissolves readily in acids, forming salts that have an acid

reaction and are bitter. Most of the salts are soluble in water, alcohol, and ether. When solutions of the salts are shaken with chloroform, the narcotine is dissolved in it, even in the presence of a free acid.

1. *Sodium hydrate* precipitates narcotine from solutions of its salts, in the form of a white crystalline powder that is insoluble in an excess of the reagent.

2. *Ammonium hydrate* precipitates narcotine in the form of a white powder that is insoluble in an excess of the reagent. If the liquid containing this precipitate is shaken with considerable ether, the ether dissolves the precipitate, and two clear layers of liquid are formed. If some of the ethereal solution is allowed to evaporate on a watch glass, the narcotine will remain as a white crystalline powder.

3. *Sodium carbonate* precipitates narcotine from its solutions in the form of a white crystalline powder that is insoluble in an excess of the reagent.

4. *Sodium bicarbonate* gives the same reaction as sodium carbonate.

5. *Tannic acid* does not produce a precipitate in neutral solutions of narcotine salts, but sometimes gives the solution a milky appearance. If a drop of hydrochloric acid is added, a precipitate is formed that dissolves when heated, and separates again when the solution is cooled.

6. *Chlorine water* imparts a greenish-yellow color to solutions of narcotine salts. If ammonia is now added, the color is changed to reddish yellow, and becomes stronger.

7. *Concentrate sulphuric acid* dissolves narcotine, forming a solution with a greenish-yellow color that soon changes to pure yellow. If this solution is heated, various colors are produced, depending on the amount of narcotine present. If considerable narcotine is present, the solution at first assumes an orange color, then becomes blue, and sometimes purple streaks form. If the solution is now allowed to cool, it assumes a red color, but if heated nearly to boiling, it becomes reddish violet. If the sulphuric acid contains but very little narcotine, a crimson color is seen instead of blue.

8. If a little narcotine is dissolved in concentrate sulphuric

acid, and heated until it assumes a reddish color, and, after cooling, a drop of ferric chloride is added, at the point where the ferric chloride enters the liquid a red color is formed that shades off to violet; after about 10 minutes, the red color spreads to the rest of the liquid.

9. *Nitric acid* of 1.4 Sp. Gr. dissolves narcotine to a reddish-yellow solution. During the solution, heat is generated and reddish fumes are evolved. If the solution is now heated over the Bunsen flame, more fumes are given off, and the solution becomes clear yellow.

10. A solution containing 10 milligrams of ammonium molybdate in 1 cubic centimeter of concentrate sulphuric acid dissolves narcotine to a green solution that rapidly changes to red.

104. Separation of Quinine, Cinchonine, and Narcotine.—If an acid solution of these alkaloids is shaken with chloroform, the narcotine will be dissolved in the chloroform and form a separate layer of clear liquid, while the quinine and cinchonine remain in the acid solution. If the chloroform solution is removed and evaporated in the air, the narcotine remains as a white powder. Now render the solution, containing quinine and cinchonine, alkaline with ammonia, and shake it with ether that contains about 2 per cent. of alcohol. This will precipitate the cinchonine, and dissolve the quinine, which may be obtained in the same manner as the narcotine. The precipitated cinchonine may then be obtained from the liquid.

GROUP III.

Non-volatile alkaloids that are precipitated by sodium hydrate, and are insoluble in an excess of the reagent, but are not precipitated from acid solutions by sodium bicarbonate.

Strychnine *Brucine* *Atropine*

105. Strychnine.—Strychnine is an exceedingly poisonous, white crystalline substance found in various varieties of strychnos, but especially in the beans of the strychnos nux

vomica. It has an alkaline reaction, and is very bitter. It is almost insoluble in water, alcohol, or ether, but dissolves in chloroform and acetic ether. It neutralizes acids, forming salts, most of which are soluble in water and alcohol, but are insoluble in ether and chloroform. They all have an extremely bitter taste, and are exceedingly poisonous.

1. *Sodium hydrate* precipitates strychnine from solutions of its salts, in the form of a white crystalline powder that is insoluble in an excess of the reagent. If the solution is very dilute, the precipitate only separates after some time.

2. *Ammonium hydrate* precipitates strychnine in the form of a white powder that is soluble in an excess of the reagent. But if this solution is allowed to stand for some time, it again separates, in the form of white needles.

3. *Sodium carbonate* gives the same reaction as sodium hydrate.

4. *Sodium bicarbonate* slowly precipitates strychnine from neutral solutions, in the form of fine white needles that are insoluble in an excess of the reagent. But, if a drop of acid is added, the precipitate dissolves in the carbonic acid that is liberated, even if the solution remains alkaline. In acid solutions, sodium bicarbonate produces no precipitate.

5. *Tannic acid*, when added to a solution of a strychnine salt, produces a white precipitate that is insoluble in hydrochloric acid.

6. *Chlorine water*, when added to a solution of a strychnine salt, produces a white precipitate that dissolves in ammonia to a colorless solution.

7. *Mercuric chloride*, added to a solution of a strychnine salt, produces a white precipitate that dissolves when heated, and is reprecipitated in white needles upon cooling.

8. *Potassium sulphocyanide*, when added to a strong solution of a strychnine salt, produces a white crystalline precipitate that is only slightly soluble in an excess of the reagent. In dilute solutions this precipitate is only formed after standing for some time.

9. *Cerium dioxide*, when added to a solution of strychnine

in concentrate sulphuric acid, produces a deep-blue color that slowly changes to violet, and finally to red.

10. *Concentrate sulphuric acid* dissolves strychnine to a colorless solution. If, to a little of this solution in a porcelain dish, a little dry potassium chromate is added, it imparts a blue color to the solution that changes to red, and finally to reddish yellow. The same reaction is produced by manganese dioxide, but, in this case, it takes place more slowly. This reaction may be varied in several ways. If a solution, made by dissolving 10 milligrams of potassium chromate in 5 cubic centimeters of water, and adding 15 grams of concentrate sulphuric acid, is placed in a test tube, and a solution of strychnine is added, so that it forms a separate layer, a bluish-violet band will be formed where the two liquids come in contact. The same reaction is obtained if a little solid strychnine or one of its salts is sprinkled on the acid-chromate solution. Morphine, if present, interferes with this reaction. This may be partly overcome by placing a few small particles of the strychnine on a watch glass, covering with a dilute solution of potassium dichromate, and stirring well. By this means the strychnine is slowly converted into strychnine chromate, which is almost insoluble. Pour off the liquid, wash the residue once with water, pour off as much of this as possible, and absorb the rest with a piece of filter paper. By this treatment the strychnine chromate is obtained as a solid in the dish, and most of the morphine is removed, if only a small amount was present. Now, if a little concentrate sulphuric acid is brought into the dish, bluish-violet streaks are formed. The best method of obtaining this reaction when morphine is present is to treat the concentrate aqueous solution of the salts with potassium chromate, when the strychnine will be precipitated as strychnine chromate, and the morphine will remain in solution. Filter the strychnine chromate, wash at once with cold water, and dry it. If the dry precipitate is rubbed off the paper into a porcelain dish, and treated with concentrate sulphuric acid, a bluish-violet color is produced at once.

11. *Nitric acid* of 1.4 Sp. Gr. dissolves strychnine to a

colorless solution that turns yellow when heated. A little potassium chlorate added to the cold colorless solution gives it a purple color.

106. Brucine.—Brucine is a white crystalline substance found associated with strychnine in the strychnos nux vomica. It is but slightly soluble in water or ether, but dissolves readily in alcohol. It is very poisonous, and is extremely bitter. It neutralizes acids completely, forming salts that dissolve readily in water. Like the free alkaloid, the salts are poisonous and very bitter.

1. *Sodium hydrate* precipitates brucine from solutions of its salts in the form of a white, granular, or crystalline precipitate that is insoluble in an excess of the reagent.

2. *Ammonium hydrate* produces a white precipitate that at first has an oily appearance, but becomes crystalline upon standing. When first precipitated this is soluble in an excess of the reagent, but if the solution thus obtained is allowed to stand for some time, the precipitate again separates in the form of crystals that do not dissolve in more of the reagent.

3. *Sodium carbonate* produces the same reaction as sodium hydrate.

4. *Sodium bicarbonate* produces a white, silky precipitate of brucine, which is insoluble in an excess of the reagent, but is dissolved by a drop of acid.

5. *Tannic acid* produces a dirty white precipitate that is insoluble in hydrochloric acid, but dissolves in acetic acid.

6. *Chlorine water*, when carefully added to the solution of a brucine salt, imparts a bright-red color to the solution. If ammonia is now added, the color changes to brownish yellow. If a little chlorine water is added to solid brucine, it dissolves to a red liquid that becomes colorless if more chlorine water is added. If this colorless solution is evaporated to dryness on the water bath, it deposits a red residue.

7. *Mercuric chloride*, added to a solution of a brucine salt, produces a white, granular precipitate.

8. *Mercurous nitrate* that contains as little free acid as possible, when added to the solution of a brucine salt, leaves

the solution colorless. But if this is now gently heated on the water bath, it gradually assumes a red color. This reaction serves well to detect brucine in the presence of strychnine, which is not colored by mercurous nitrate.

9. *Potassium sulphocyanide*, when added to a strong solution of a brucine salt, produces a white, granular precipitate. The same precipitate separates from more dilute solutions after standing some time.

10. *Concentrate sulphuric acid*, when added in small amounts to a little brucine, dissolves it, forming a rose-colored solution that soon changes to yellow. If a little sulphuric acid containing nitric acid* is added, the liquid at first assumes a red color that soon changes to yellow.

11. *Concentrate nitric acid* dissolves brucine and its salts to bright-red solutions that soon change to yellowish red, and, when heated, become yellow. If stannous chloride is added to a solution that has been heated until it is yellow, it assumes a deep-violet color, and, if the solution is concentrate, a violet precipitate separates. The violet color will be imparted to solutions that have been quite largely diluted with water. Colorless ammonium sulphide produces the same reaction as stannous chloride, and hydrogen sulphide produces a violet color at first, but, upon continued treatment, the solution finally becomes green.

12. If a little brucine is dissolved in acetic acid, the solution diluted with water, and lead dioxide added, a rose color is imparted to the liquid.

107. Atropine.—Atropine is a white crystalline substance found in the deadly nightshade. It is only slightly soluble in water or ether, but dissolves readily in alcohol and chloroform. It is poisonous, has a bitter taste that is very persistent, and an alkaline reaction. It unites with acids, forming salts that are easily soluble in water or alcohol, but insoluble, or nearly so, in ether.

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* This mixture of acids, known as *Erdmann's acid mixture*, is made by mixing 6 drops of strong nitric acid with 100 cubic centimeters of water, and adding 10 drops of this mixture to 20 grams of concentrate sulphuric acid.

1. *Sodium hydrate* precipitates part of the atropine from strong aqueous solutions of its salts, in the form of a white powder, that is insoluble in an excess of the reagent.

2. *Ammonium hydrate*, added to a rather strong solution of an atropine salt, produces a white precipitate that is soluble in an excess of the reagent.

3. *Sodium carbonate* gives the same reaction as sodium hydrate.

4. *Sodium bicarbonate* does not produce a precipitate in a solution of an atropine salt.

5. *Gold chloride*, when added to an aqueous solution of an atropine salt, produces a yellow precipitate that gradually becomes crystalline upon standing.

6. *Tannic acid*, added to an aqueous solution of an atropine salt, produces a white, curdy precipitate that is soluble in hydrochloric acid and in ammonia.

7. *Mercuric chloride*, dissolved in water, when added to a solution of atropine in alcohol, produces a yellow precipitate that changes to orange red when gently heated.

8. If a little atropine in a porcelain dish is covered with concentrate sulphuric acid, and heated until it begins to froth and turn brown, an odor similar to that of wild-plum blossoms is given off. If a small piece of potassium dichromate is now added, the odor becomes similar to that of the wild rose, and if the heating is continued, an odor similar to that of bitter almonds is given off. The odor of flowers may also be obtained by bringing a little atropine in contact with a few chromic-acid crystals, and gently heating until the chromic acid begins to turn green.

9. If atropine is mixed with concentrate sulphuric acid in a porcelain dish, and a little solid potassium nitrite is stirred into this mixture, it assumes a yellow or orange color. If a few drops of a solution of potassium hydrate in absolute alcohol are now added, the mixture assumes a reddish-violet color that soon changes to pink.

10. If a little atropine or an atropine salt in a porcelain dish is covered with fuming nitric acid, and the mixture is evaporated to dryness on the water bath, a colorless residue

remains, which assumes a violet color that changes to red, if a drop of potassium hydrate dissolved in absolute alcohol is added to the residue after it becomes cold. Strychnine and some other compounds give similar reactions, but not the same.

108. Separation of Strychnine, Brucine, and Atropine.—Strychnine may be separated from brucine and atropine by shaking these alkaloids with cold absolute alcohol, when the brucine and atropine will be dissolved, and the strychnine, which is insoluble in cold absolute alcohol, may be filtered off. Brucine and atropine may be separated by shaking an alkaline solution containing them with petroleum ether, which dissolves the brucine, and leaves the atropine. The brucine may be obtained by separating the layer of petroleum ether, and evaporating it at a rather low temperature. If the solution, separated from the petroleum ether, which contains the atropine, is shaken with ether, the atropine will be dissolved, and may be obtained by separating the ethereal solution and evaporating it in the air.

Strychnine and brucine occur together in nature, and are often found together in commerce. When only these two alkaloids are present, they may be separated by placing the dry substance in a porcelain dish, and covering it with strong chlorine water, when brucine will be dissolved to a red solution, and the strychnine will remain unchanged.

QUANTITATIVE ANALYSIS.

(PART 1.)

INTRODUCTION.

1. Definition of Quantitative Analysis.—Quantitative analysis is that branch of chemistry which has for its object the study of the methods for the determination of the exact quantities of the different constituents of a substance. If it is required to merely ascertain the amount of one of the elements contained in a substance, the operation is called a *determination*. If the amount of each of the elements is required, the process is called an *analysis*. Qualitative analysis informs us what elements a substance contains, without reference to quantity; and quantitative analysis takes the subject up where qualitative analysis leaves it, and shows us the exact amount of each of these elements contained in the substance. For instance, by means of qualitative analysis we learn that a silver coin is composed of silver and copper, and, by noting the relative sizes of the precipitates obtained, we would judge that it contains more silver than copper, but more than this we cannot learn from qualitative analysis. Having learned by qualitative analysis that the coin is composed of silver and copper, we are now ready to subject it to a quantitative analysis, and by this means determine the exact amount of each of these elements that it contains. Obviously, the qualitative analysis precedes the quantitative, for we must know what elements a substance contains before we determine their amount.

The methods employed to obtain these results vary greatly, and are based on different principles. Depending on the principles employed, the subject may be divided into three parts; viz., *gravimetric analysis*, *volumetric analysis*, and *special methods*.

2. Gravimetric Analysis.—In gravimetric analysis, as the name implies, the elements are determined by separating and weighing them. They may be precipitated and weighed in the uncombined state, in which case they are known as *educts*, or they may be precipitated in the form of compounds of known composition, known as *products*. The weight of an educt is, of course, the weight of the element contained in the sample, while in the case of a product, the quantity of an element that this known compound contains must be calculated. This may be illustrated very well by means of the coin above referred to. If 1 gram of the silver coin were dissolved in nitric acid, and the copper precipitated from this solution by means of a current of electricity, the educt thus obtained would weigh .1 gram, or one-tenth the weight of the coin. Thus we find directly that the coin contains 10 per cent. of copper. If the copper should be precipitated and weighed in the form of oxide CuO, the weight of this product would be .1254 gram, and from this the weight of the copper would have to be calculated. As the composition of the product is known, this may easily be done by making use of the proportion:

$$\text{Mol. Wt. } CuO : \text{At. Wt. } Cu = \text{Wt. of product} : x.$$

Taking the atomic weights of copper and oxygen as 63 and 16, respectively, and substituting the values in the above proportion, we obtain:

$$79 : 63 = .1254 : x. \quad x = .1 \text{ gram of copper.}$$

The percentage of the elements in the compounds most frequently weighed, has been ascertained by experiment and calculation, and the results thus obtained have been published in the form of so called "tables for the calculation of analyses"; in actual analysis, these are generally used in

calculating results. By multiplying the weight of the product by the percentage of the element sought, and dividing by the weight of sample taken, the percentage of the element contained in the original substance is obtained directly. If the atomic weights of copper and oxygen are taken as 63 and 16, respectively, copper oxide will contain 79.75 per cent. of copper. Using this in the above example, we would have $.1254 \times 79.75 \div 1 = 10$ per cent. of copper in the coin.

From what has been said, it is evident that in gravimetric analysis the element to be determined must either be weighed as an educt or converted into an insoluble compound that is of known composition and is capable of being weighed exactly. The terms *soluble* and *insoluble* are always used relatively in chemistry. No compound is soluble to an indefinite extent, and no compound is absolutely insoluble. When an insoluble compound is spoken of in quantitative analysis, a compound is meant that does not dissolve to any appreciable extent in the quantity of liquid ordinarily present. The compound into which the element is converted must be one that can be weighed exactly. If the element is converted into a compound that absorbs moisture so rapidly that it cannot be accurately weighed, we have no means of determining its amount; and however accurately a compound may be weighed, if its composition is not known, we have no means of calculating the quantity of the desired element that it contains.

3. Volumetric Analysis.—In volumetric analysis, the quantity of an element in a substance is determined by noting the quantity of a liquid of known power of action required to change the element from one definite state to another equally definite state. In doing this it is necessary that we have the means of determining the exact point at which the reaction is complete. Returning to the illustration of the coin, the silver may be precipitated from the solution by a solution of sodium chloride, according to the equation:

$$AgNO_3 + NaCl = NaNO_3 + AgCl$$

the silver chloride weighed, and the silver calculated as in the

case of the copper. But in this case we may determine the silver volumetrically, for we know that 1 molecule of sodium chloride changes 1 molecule of silver nitrate to 1 molecule of silver chloride. Consequently, if we add just enough of a solution of sodium chloride of known strength to precipitate all the silver from the solution, we can readily calculate the amount of silver present from the amount of sodium chloride required to precipitate it. But volumetric analysis is not limited to precipitations. We have seen that oxidizing agents change some of the metals from lower to higher states of oxidation. Thus, potassium permanganate changes ferrous to ferric compounds, according to the equation:

$$10FeSO_4 + 8H_2SO_4 + 2KMnO_4$$
$$= 5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + 8H_2O$$

Now, if we add a potassium-permanganate solution of known strength to a ferrous sulphate solution containing free sulphuric acid, the color of the permanganate is destroyed while oxidation is taking place; but, finally, a point is reached at which an additional drop of the permanganate imparts a permanent pink color to the solution, showing that the oxidation is complete. Knowing the strength of the permanganate solution, and the amount used, we can readily calculate the quantity of iron oxidized from the above equation. This method of analysis is peculiarly adapted for the determination of free acid or alkali in a solution. If we wish to determine the strength of a solution of hydrochloric acid, all that is necessary is to add a few drops of phenol-phthalein solution, and then slowly introduce a solution of sodium hydrate, the strength of which is known, until the last drop gives a permanent reddish tinge to the solution, showing that the acid has been neutralized. Knowing the quantity and strength of the sodium-hydrate solution used, the amount of acid may readily be calculated from the equation:

$$HCl + NaOH = NaCl + H_2O$$

Thus, we see that the volumetric method of analysis is widely applicable, and may be used in every case where a solution of known strength acts quantitatively on another solution in

ıch a way that the exact point at which the reaction is com-
lete may be noted.

4. Special Methods.—Under this head are grouped ıose methods that are based on principles differing from hose mentioned above. To this class of analyses belong the o called colorometric methods, in which the quantity of a sub-tance in a solution is determined by comparing the color of he unknown solution with the color of a solution of known strength. The determination of substances by means of the polariscope, in which the quantity of a substance present in a solution is determined by the extent to which the solution polarizes light, also belongs to this class of analyses.

5. Importance and Scope of Quantitative Analysis.—We can hardly overestimate the importance of quantitative analysis. In fact, it may be said that chemistry owes its elevation to the rank of a science to this branch, for it was through quantitative investigation that the laws on which the science is founded were discovered. Quantitative researches revealed the composition of chemical compounds, and from these the laws that govern chemical combinations and transpositions were deduced. The field of quantitative analysis is practically limitless. All material bodies—solid, liquid, or gaseous—may be subjected to quantitative investigation. The field is so broad that it cannot be covered by a work of this character, so in this Course only those substances that are necessary to give the student a thorough knowledge of the methods employed, and those that frequently call for analysis, will be treated. If, however, the student masters what is here given, he will be able to perform ordinary operations and will be in a position to pursue the study of any particular branch of the subject. The subject as treated in this Course may be divided into two parts; viz., the analysis of chemical compounds and the analysis of complex substances. The objects in these two cases are different. Complex substances are usually analyzed in order to render a service to one of the industries, while the analysis of chemical

compounds is primarily for the purpose of solving questions relating to chemical theory. In beginning quantitative analysis, the student should always determine the elements in a number of compounds of known composition before attempting the analysis of complex substances, as by this means he will become familiar with quantitative methods and the properties of precipitates, and will be able to ascertain the correctness of his results by simple calculations. On account of its many advantages, this system will be followed in the present work.

6. Preparation of the Sample for Analysis.—In the analysis of minerals and many industrial products, the sample must be finely pulverized and dried before weighing it for analysis. It is usually broken into small pieces by some convenient method, and these pieces are then ground to a fine powder, generally by means of a mortar and pestle made of agate. The ground sample is then dried by heating it for an hour or so in an air bath, similar to the one shown in Fig. 1, at a temperature generally ranging from 100° to 115°. The bath should be provided with a thermometer *a*, and the temperature may be regulated by turning the burner *b* up or down, as the case may require.

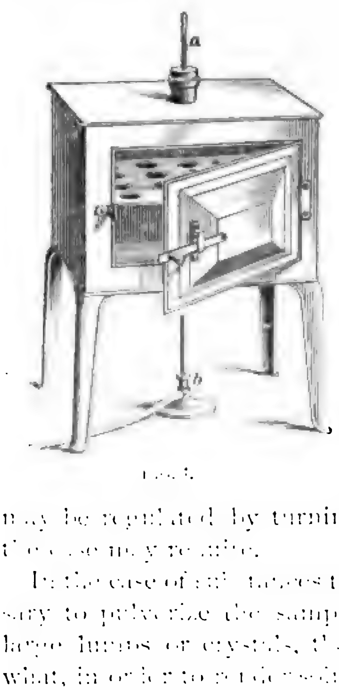

Fig. 1.

In the case of substances that dissolve easily, it is not necessary to pulverize the sample, but if the sample consists of large lumps or crystals, these should be broken up somewhat, in order to render the solution more easy and rapid. Compounds must also be dried to remove hygroscopic moisture; but, in the case of those containing water of constitution, or crystallization, this must be done very carefully in order to

avoid the removal of water that properly belongs to the compound. Unless a crystalline substance is quite damp, it should not be heated in an air bath at all, but should be dried by a method to be described later. If the sample is quite damp, it must be dried by allowing it to stand in warm air or in the air bath. A few minutes' heating at a moderate temperature is usually sufficient to remove the hygroscopic moisture in these cases, but the student will have to rely largely on his own judgment in this matter. In any case, the dried sample should be allowed to cool in a desiccator to prevent the absorption of moisture from the air while cooling.

A convenient form of desiccator is shown in Fig. 2. In the bottom is placed dry fused calcium chloride, which absorbs the moisture rapidly, rendering the air in the dessicator perfectly dry. A pipestem covered triangle, or still better, a platinum-covered triangle—which may be made by wrapping platinum foil around an ordinary iron triangle—is placed at the narrow portion to support the watch glass containing the sample or the crucible containing the precipitate to be weighed.

FIG. 2.

Salts containing water of crystallization must not be allowed to remain long in the desiccator, as they gradually give up their water of crystallization in this dry air—a fact indicating the best method of drying crystalline substances that are not too damp. The salt containing water of crystallization is merely placed in a desiccator and allowed to stay there until the hygroscopic moisture is absorbed; it is then removed and weighed before it begins to lose water of crystallization. No fixed rules can be given for the length of time crystalline substances should remain in the desiccator, but the student will soon learn this by practice. In the case of copper sulphate and similar substances, the drying should be stopped as soon as the compound begins to show any change in crystalline form or color, and only those crystals

that have not been changed in any way by the drying process should be selected for analysis.

7. Weighing.—Weighing is one of the most important operations in quantitative analysis, as all results depend on this operation. In every analysis, the sample must be weighed. In gravimetric analysis, the educts or products are also weighed, and in volumetric analysis, the substances used in making the *standard solutions* are weighed; hence, the accuracy of all quantitative work depends largely on accuracy in weighing. The process of weighing has been described in Arts. **17** and **18**, *Theoretical Chemistry*, and the balance and method of using it there described will be found sufficiently accurate for practice and for many practical analytical processes; but if exact weighing is required, a balance similar to that shown in Fig. 3 must be employed.

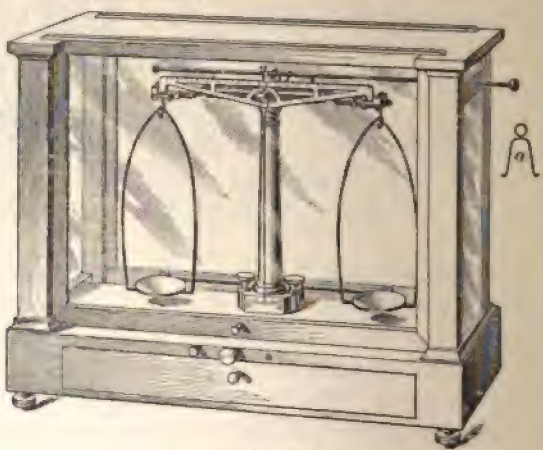

FIG. 3.

In this case, a 10-milligram weight is the smallest one placed upon the pan of the balance. The weights are added as described in Art. **18**, *Theoretical Chemistry*, until an additional 10-milligram weight is too much. Then place the centigram rider *a*, Fig. 3, on the beam, and move it from place to place until a point is found at which the pointer vibrates an equal distance on each side of the zero poi

m is so graduated that the same effect is produced ng the rider on these graduations as would be pro- y placing weights varying from $\frac{1}{10}$ of a milligram to grams on the pan.

ever form of balance is used, a few simple rules lways be followed.

nly a very few substances should ever come in con- 1 the pans of the balance. The number of substances ierally be limited to three; viz., glass, metals, and a. If chemicals are weighed directly on the pans, l almost invariably be corroded; hence, samples for should be weighed on a watch glass, and the pro- ould be weighed in crucibles. In weighing samples tch glass, the watch glass is usually rinsed with cold riped well on a soft, dry cloth, and weighed. The s now added, and the weight of the glass and sample By subtracting the first weight from the second, the of the sample is obtained. Some chemists, however, o heat the watch glass carefully over the Bunsen d allow it to cool in a desiccator before weighing.

he pans of the balance should always be arrested hanging weights, and this should be done carefully, den jar injures the balance.

vessel should never be weighed while warm, for in e it will always weigh lighter than it really is.

heoretically, it is immaterial upon which pan a sub- s weighed, but in practice, it is best to always weigh e same pan of the balance. As a rule, the substance ighed is placed upon the pan to the left of the oper- ie sits facing the balance, and the weights are placed e pan to his right.

rdinarily, samples are weighed on a watch glass as sly described, but this method cannot be used in the deliquescent substances, as they attract moisture, is increase in weight very rapidly. Consequently, bstances should be weighed in a light, tightly stop- lass tube, the tube removed from the balance, a quantity of the substance shaken into the vessel in

which the analysis is to be performed, the stopper quickly replaced, and the tube and substance remaining in it again weighed. The difference between the two weights, of course, represents the substance taken for analysis.

8. The Use of Reagents.—In quantitative analysis, all the operations must be performed with greater care than is required in qualitative analysis, as a small addition or loss of substance causes a serious error in the result. This is particularly true of the use of reagents. Enough of the reagent must always be added to completely precipitate the element to be determined, but a large excess must be avoided, as in some cases an excess of the reagent tends to redissolve the precipitate at first formed, thus rendering the result obtained too low. In other cases, if an excess of the reagent is added, it persistently adheres to the precipitate so that it can only be washed out with difficulty, and if not thoroughly removed, it gives too high a result. While this is an important matter in single determinations, it is of still greater importance in complete analyses, where the elements are successively removed from a solution by means of reagents. Take, for example, the analysis of limestone, in which silica, iron and aluminum, calcium, and magnesium are usually determined. If a large amount of free hydrochloric acid is left in the solution when the silica is removed, a large amount of ammonia will be required to neutralize the solution before the iron and aluminum are precipitated, and much ammonium chloride will thus be formed in the solution. The next step in the analysis is the removal of calcium by means of ammonium oxalate, and if a large excess of this is also used, we will find by the time that we come to precipitate the magnesium as magnesium-ammonium phosphate, that the solution contains so large a quantity of salts introduced by reagents that this cannot be done, and the analysis will be lost. The ammonium chloride alone would prevent the complete precipitation, and the result obtained would be erroneous. It must be remembered that water is in a sense a reagent, and its excessive use is to be

avoided. On the other hand, enough of each reagent must be added to completely precipitate the elements, or the results obtained will be equally useless and misleading.

It is not so difficult a matter as it may appear, to determine the proper quantity of a reagent to be added, for in the analysis of salts the proper amount may readily be calculated, and after analyzing a few of these the student will learn to recognize the point at which precipitation is complete. The method of calculating the quantity of a reagent required may be illustrated by taking the case of the determination of chlorine in common salt. In this determination, the chlorine is precipitated in the form of silver chloride by silver nitrate, according to the equation:

$$\underset{58.36}{NaCl} + \underset{169.55}{AgNO_3} = \underset{143.03}{AgCl} + \underset{84.88}{NaNO_3}$$

If .5 gram of sodium chloride is taken for analysis, the weight of silver nitrate necessary to precipitate the chlorine may be calculated by means of the proportion:

$$58.36 : .5 = 169.55 : x. \quad x = 1.45 \text{ grams.}$$

If the reagent contains 20 grams of silver nitrate in 500 cubic centimeters of solution, the volume of reagent required may be obtained by means of the proportion:

$$20 : 1.45 = 500 : x. \quad x = 36\tfrac{1}{4} \text{ cubic centimeters.}$$

In practice, it will be found that a little more than the calculated amount of a reagent will be required to produce complete precipitation; hence, 1 or 2 cubic centimeters more than the calculated amount should always be added. In the case of precipitates that settle quickly, a drop or two of the reagent should be added to the clear liquid above the precipitate before filtering, and, as an extra precaution, a few drops of reagent should always be added to the filtrate. If this produces a precipitate, the addition of reagent must be continued as long as a precipitate forms, and this must be filtered off and added to the main precipitate.

9. Filtering.—Filtration has been described in Art. **99**, *Theoretical Chemistry*, and the general method there described should be followed; but in quantitative analysis,

greater care must be taken in filtering than was necessary in any of the preceding work. The ordinary filter paper generally used in qualitative work cannot be used here, as the ash is so heavy that it seriously affects the results. A large number of brands of specially prepared filter paper are for sale by chemical dealers, and of these the Swedish paper is probably the best. Most of these specially prepared papers leave so little ash when burned, that it may be disregarded in all ordinary work. They may be obtained in disks of various sizes. A size should be chosen that, when folded and placed in the funnel, reaches nearly to the top of the latter, but does not protrude beyond its edges. For ordinary quantitative work, the funnels should be of glass. The filter should be fitted closely into the funnel, a little water added, and the paper pressed closely to the sides of the funnel. If this is properly done, the air cannot pass between the paper and glass, and the funnel tube will contain a column of water, the weight of which tends to draw the liquid through the paper, rendering filtration much more rapid than it would be otherwise. In cases where only a single element is to be determined, filtration is rendered more rapid by bending a piece of glass tubing the size of the tube of the funnel, so that a ring is formed near its upper end, and fastening this to the tube of the funnel by means of a piece of rubber tubing, as shown in Fig. 4. The longer column of liquid thus obtained draws the liquid through the filter much more rapidly than the short column before described, and thus saves much time. This method should not be employed when more than one of the elements in a solution is to be determined, as there is always greater danger of losing some of the filtrate when it is employed. When more than one element is to be determined, the tube of the

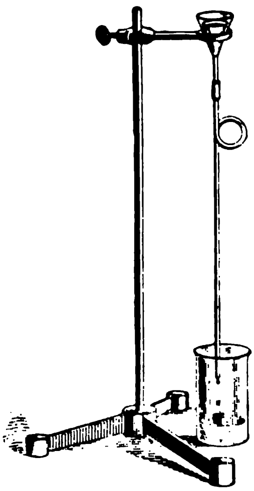

FIG. 4.

funnel should rest against the side of the beaker in which the filtrate is received, so that the filtrate runs down the side of the glass and thus avoids spattering. The greatest care should be taken in this case to avoid any loss of, or addition of foreign substance to, the filtrate.

In nearly every case, small particles of the precipitate will adhere so persistently to the sides and bottom of the vessel in which the precipitation was made, that a jet of water from the wash bottle fails to remove them. These particles are usually loosened by means of an instrument known as a "policeman," made by placing a short piece of soft rubber tubing on the end of a glass rod, as shown in Fig. 5. After rubbing the precipitate from the sides and bottom of the vessel in this way, it may be washed on to the filter by a jet of water from the wash bottle. Any particles clinging to the policeman must also be washed on to the filter. This rod, or at least the end having the rubber, should never be used to stir solutions, or for any purpose except to remove precipitates from vessels. Small quantities of some precipitates adhere so closely to the vessels that they cannot be removed by the policeman. In these cases, after removing as much as possible of the precipitate to the filter, the remaining particles must be dissolved in a few drops of acid, a little water added, the substance reprecipitated by a slight excess of the original reagent, and this precipitate added to the main precipitate on the filter.

FIG. 5.

10. Recording Analyses.—A careful and complete record of all analyses performed should be kept in a book which is used for this purpose alone. Each weight should be set down in this book as soon as taken. The weight of the watch glass should first be set down, the weight of the watch glass plus the sample placed directly above this, and the weight of the sample is then obtained by subtracting the first weight from the second. The weight of the crucible is next set down, the weight of the crucible plus the precipitate is placed directly above this, and the weight of the precipitate

obtained by subtraction, as in the case of the sample. A uniform method of recording analyses should be adopted, and the following form, which has been found very convenient, is recommended for recording the gravimetric determination of single elements in compounds.

DETERMINATION No........

Determination of..............*in*..............*by*............*method.*

Commenced............................

Watch glass + substance	=	....
Watch glass	=	....
Substance	=	....
Crucible + Ppt.	=	....
Crucible	=	....
Ppt.	=	....
Per cent. of.................found	=	....
Per cent. calculated	=	....
Error	=	....

CALCULATIONS AND REMARKS.

....

....

....

Completed..........................

Signed.............................

GRAVIMETRIC DETERMINATIONS.

GENERAL REMARKS.

11. It is impossible to master the subject of quantitative analysis by merely reading directions, without actually performing the operations described; hence, the student is urged to make as many of the following determinations as possible. The operations are simplified as much as possible,

so that many of them can be performed with very limited facilities. After each determination, the student should calculate the theoretical percentage of the element determined in the compound taken, and compare the result obtained with this calculated result. It will be found that the result obtained by analysis very rarely corresponds exactly with the calculated result, and when this does happen, it is only by chance. There are a number of reasons why these results do not ordinarily agree exactly. The compound analyzed may not contain exactly the theoretical amount of the element determined; or, if it does have exactly the theoretical composition, the discrepancy may be due to the method or to execution. Probably no method is absolutely correct. All substances dissolve to a greater or less extent, and those that are ignited may be partially decomposed or slightly volatilized. The execution of an analysis can never be absolutely accurate, even though the greatest care is taken. The balances are not absolutely accurate, our weights and measures are not absolutely correct, reagents are not absolutely pure, and, however careful we may be, we can never completely avoid dust. With good methods and careful manipulation, however, the results should come very close to the truth. The student is strongly advised to weigh up two samples and make duplicate determinations in each case. The best way to master this part of the work is to first read all that is given in regard to a determination, and then, using the description given as a guide, make this determination and become thoroughly familiar with it before passing on to the next element.

CHLORINE.

12. Determination of Chlorine as Silver Chloride.—Weigh very accurately about .5 gram of pure, dry sodium chloride $NaCl$ on a watch glass, carefully transfer it to a beaker, and dissolve it in about 75 cubic centimeters of water. Heat this solution gently, and precipitate the chlorine by adding slowly, and with constant stirring, a slight

excess of a solution made by adding about 10 drops of nitric acid to 40 cubic centimeters of silver nitrate. Continue the addition of this reagent until an additional drop produces no additional cloudiness in the nearly clear solution above the precipitate, which has been allowed to settle to the bottom of the beaker. Now raise the heat and continue the stirring until the liquid comes to the boiling point, and the precipitate gathers, and settles rapidly, leaving the supernatant liquid clear.

Decant as much as possible of the clear liquid through a filter, leaving the precipitate in the beaker, and to this add about 50 cubic centimeters of hot water and half a dozen drops of nitric acid. After stirring well, allow the precipitate to settle, decant the liquid through the filter, wash the precipitate on to the filter, and while it is on the filter, wash it with hot distilled water until it is free from silver nitrate. If all the water is allowed to run through each time, before another quantity is added, about five or six washings will generally be sufficient. Cover the funnel with a piece of paper to protect the precipitate from dust, and stand it aside to dry; or, better, heat it in an air bath at about 100° until it is perfectly dry.

While the precipitate is drying, heat a porcelain crucible and cover to redness on a triangle over the non-luminous flame of a Bunsen burner, allow it to cool in a desiccator, and weigh it. Remove the dried precipitate as completely as possible from the filter to a watch glass, using a small camel's-hair brush to remove the last particles. Place the filter in the weighed crucible and ignite gently at first, but gradually raising the temperature until the carbon of the paper is completely burned off, leaving a white ash. By this treatment the small amount of precipitate remaining on the paper will be reduced to metallic silver, and in order to avoid loss at this point, this must be changed back to silver chloride. To accomplish this, add 4 drops of nitric acid and 2 drops of hydrochloric acid, as soon as the crucible is cool, and heat gently until the acid is driven off. Allow the crucible and contents to cool. Add the main precipitate from the watch

glass, place the cover on the crucible, and gently heat it over the Bunsen flame until the precipitate just begins to fuse around the edges, removing the cover from time to time in order to observe when this point is reached. Remove the crucible to a desiccator, allow it to cool, and weigh it. This weight minus the weight of the empty crucible is the weight of silver chloride, and from this the percentage of chlorine is calculated. This may be done in two ways:

1. We may calculate the weight of chlorine from the atomic weights and the weight of the precipitate, by means of a proportion, and obtain the percentage of chlorine in sodium chloride by dividing the weight of chlorine thus obtained by the weight of the sample taken and multiplying by 100; thus,

Mol. wt. $AgCl$: At. wt. Cl = wt. of $AgCl : x$. x = wt. of Cl.
$x \div$ wt. of sample taken $\times 100$ = per cent. of Cl in $NaCl$.

2. We may obtain the weight of chlorine by multiplying the weight of silver chloride by the percentage of chlorine in silver chloride, which is usually given as 24.73, and dividing this result by 100; and the per cent. of chlorine in sodium chloride may be obtained by dividing this weight by the weight of the sample taken and multiplying by 100. This may be put in the following form:

$$\frac{\text{wt. of } AgCl \times 24.73}{\text{wt. of sample taken}} = \text{per cent. of } Cl \text{ in } NaCl.$$

13. Notes and Precautions.—If pure sodium chloride is not at hand, some of the crude salt may be purified by leading hydrochloric-acid gas through a saturated solution of common salt in water. As the salt is much less soluble in hydrochloric acid than in water, it soon begins to crystallize out of the solution. When considerable of the salt has separated, pour off the supernatant liquid, wash the crystals two or three times with concentrate hydrochloric acid, remove them to a watch glass, and dry them thoroughly in an air bath at from 100° to 110°.

Silver chloride is almost absolutely insoluble in water, and also in very dilute nitric acid, but in strong nitric acid it

dissolves quite perceptibly; hence, a large quantity of nitric acid should not be added to the silver nitrate used as reagent. It is also slightly soluble in alkali nitrates and in silver nitrate; hence, a large excess of reagent should be avoided. The action of light slowly reduces silver chloride, and direct sunlight accomplishes this much more rapidly; hence, the precipitate should be shielded from the light as much as possible throughout the entire process.

The salt solution should only be gently warmed until precipitation is complete, as the nitric acid contained in the reagent will invariably expel some chlorine from a hot solution during precipitation, thus causing too low a result.

The solution should be stirred with a glass rod from the time the first of the silver nitrate is added until the precipitate settles and leaves the supernatant liquid clear, as stirring causes the precipitate to collect and settle much more rapidly than it would otherwise.

The precipitate must be washed on the filter with hot water until all impurities are removed. As silver nitrate is usually the last to remain in the precipitate, we may assume that the precipitate is clean when this is all removed. To test for silver nitrate, collect 1 or 2 cubic centimeters of the washings in a test tube, by placing it under the funnel, and add to this a few drops of hydrochloric acid. If a cloudiness is produced, it shows that silver is present, and the washing must be continued until the washings give no reaction with hydrochloric acid. A few drops of silver nitrate should always be added to the filtrate to make sure that all the chlorine has been precipitated. If this causes a precipitate, the addition of silver nitrate must be continued as long as a precipitate forms, and the precipitate thus formed must be added to the main precipitate.

For handling hot crucibles, nickel crucible tongs are to be recommended; but, if these are not available, perfectly clean steel forceps may be used.

In transferring precipitates from filter paper to watch glass, and from watch glass to crucible, the watch glass and crucible should always stand on a piece of perfectly clean

glazed paper, so that any particles falling upon the paper may be brushed into the vessel intended to receive them.

The silver chloride always adheres to the crucible with greater or less persistence, and this is especially true if the ignition has been carried too far. To clean the crucible, remove the loose portion of the precipitate, place a little zinc in the crucible, and add some dilute hydrochloric acid. The nascent hydrogen generated reduces the chloride, and after a few minutes the precipitate may be easily removed.

IRON.

14. Determination of Iron as Oxide.—Weigh up accurately about 1.5 grams of ferrous ammonium sulphate $Fe(NH_4)_2 2SO_4, 6H_2O$, which has been previously dried for a few minutes in a desiccator if necessary, transfer it to a beaker, and dissolve it in 150 cubic centimeters of water and 1 cubic centimeter of hydrochloric acid. Heat the solution to boiling and add concentrate nitric acid, a few drops at a time, until the solution assumes a clear reddish-yellow color, showing that the iron has been oxidized from the ferrous to the ferric condition, but taking care to avoid a large excess of nitric acid. When oxidation is complete, add ammonium hydrate to the boiling liquid, drop by drop, and with constant stirring, until the iron is completely precipitated and the liquid remains slightly alkaline, but avoiding a large excess of ammonia. Continue the boiling for about a minute, and take care that the liquid remains slightly, but distinctly, alkaline. Remove the beaker from the flame, and as soon as the precipitate settles, pour as much of the clear liquid as possible through a filter, and wash the precipitate once or twice by decantation with hot water. Then bring the precipitate on to the filter, and wash it with hot water until 2 or 3 cubic centimeters of the washings in a test tube fail to give a precipitate with barium chloride. Cover the funnel with a piece of paper to protect the precipitate from dust, and stand it in an air bath, or in some warm place, to

dry. Remove the dried precipitate as thoroughly as possible from the filter to a watch glass, by rubbing the sides of the filter together and using a camel's-hair brush. Place the filter in a weighed platinum or porcelain crucible, and ignite it over the Bunsen burner until the carbon is completely burned off. After allowing it to cool, add the main precipitate, and again ignite, first at a gentle heat, over the Bunsen burner, but finally for 10 minutes at the highest temperature of the blast lamp. If a blast lamp is not available, quite accurate results may be obtained by igniting the precipitate for half an hour at the highest temperature obtainable with a Bunsen burner. Allow the crucible and contents to cool, weigh, and obtain the weight of ferric oxide Fe_2O_3 by subtracting the weight of the empty crucible from this weight. The percentage of iron in the ferrous ammonium sulphate may be obtained by multiplying the weight of Fe_2O_3 by 70, and dividing the result by the weight of sample taken; or, the weight of iron may be obtained from the proportion:

$$Fe_2O_3 : Fe_2 = \text{wt. } Fe_2O_3 : x. \quad x = \text{wt. of } Fe.$$

The percentage of iron may be obtained by dividing the weight of iron by the weight of sample taken, and multiplying this result by 100.

15. Notes and Precautions.—Care should be taken to get a sample that is dry, but has not lost water of crystallization. If the sample has been kept in a dry place, it will usually be ready for analysis; if damp, it should be dried in a desiccator for a few minutes, but the drying must be stopped as soon as the salt shows any change of color, and any crystals that are coated with white, or have white spots, must be rejected.

Enough nitric acid must always be added to completely oxidize the iron, but a large excess is to be avoided. If the iron is not all oxidized, the ammonia will precipitate a mixture of ferrous and ferric compounds of unknown composition.

The precipitate of ferric hydrate must be thoroughly washed, even if no fixed compounds are present; for, if

ammonium chloride remains in the precipitate, ferric chloride will be formed and volatilized during ignition.

The precipitate formed when ammonia is added to a ferric solution is ferric hydrate, and this is changed to ferric oxide by ignition. Consequently, the precipitate must be heated to a high enough temperature to drive off the water, and the ignition must be continued until the water is all expelled. This is best accomplished by heating over the blast lamp; but in the absence of a blast lamp, the same end may usually be attained by continued heating at the highest temperature obtainable with a Bunsen burner. For many of the operations in quantitative analysis, a blast lamp is required.

COPPER.

16. Determination of Copper as Oxide.—Weigh up about 1 gram of pure crystallized copper sulphate $CuSO_4, 5H_2O$, which has been dried in a desiccator if necessary, transfer it to a porcelain dish having a capacity of about 500 cubic centimeters, dissolve in about 250 cubic centimeters of water, and heat to gentle boiling. To the gently boiling solution, add slowly, and with constant stirring, enough sodium hydrate to completely precipitate the copper, taking care to use but a slight excess of the reagent. The precipitate at first formed is blue copper hydrate; in the boiling solution, however, this is changed almost immediately to dark brown or black copper oxide. Continue the boiling for 5 or 10 minutes, with frequent stirring, until the precipitate assumes a uniform color and texture. Allow the precipitate to settle, decant the clear supernatant liquid through a filter, add hot water to the precipitate, bring it to boiling, and decant this through the filter. Wash again by decantation with hot water, and then bring the precipitate on to the filter, and wash thoroughly on the filter with hot water. Dry the precipitate, remove it as thoroughly as possible from the filter to a watch glass, and burn the filter in a weighed porcelain crucible. After the crucible has become cool, add a drop of concentrate nitric acid to the ash, and heat cautiously

until the residue is perfectly dry. Allow the crucible to cool, add the precipitate from the watch glass, cover the crucible, and heat over the Bunsen burner, gently at first, but gradually raising the temperature until it is finally ignited for 5 or 10 minutes at full redness. Cool in a desiccator, and weigh as copper oxide CuO. From this weight, calculate the percentage of copper in the copper sulphate. The proportion for calculating the weight of copper is

$$CuO : Cu = \text{wt. of } CuO : x.$$

The percentage of copper in CuO is about 79.82, and this factor is generally used.

17. Notes and Precautions.—Sodium carbonate may be used instead of sodium hydrate to precipitate copper, and it is preferred by many chemists; but, if used, the boiling must be continued for at least half an hour, and the water thus evaporated must be replaced from time to time.

Copper hydrate and copper oxide are dissolved only to a very slight extent by water or very dilute sodium hydrate, but strong sodium hydrate dissolves the precipitate quite perceptibly; hence, a large excess of the reagent should be avoided.

It frequently happens that particles of this precipitate adhere so tenaciously to the dish that they cannot be removed mechanically. In this case, dissolve the adhering precipitate in a few drops of nitric acid, add a few cubic centimeters of water, and precipitate the copper with a slight excess of sodium hydrate. Boil, wash well with hot water, as in the case of the main precipitate, filter through a very small filter paper, wash with hot water, dry, and ignite this paper and particles of precipitate adhering to it with the first filter paper.

Some of the reagent is always carried down with the precipitate, and adheres to it very persistently; but this may be removed by thorough washing with hot water. If the precipitate is not thoroughly washed, some of the sodium hydrate will remain in it and be weighed as copper oxide, making the result too high. On the other hand, if the solution is not sufficiently dilute, or if a large excess of the

reagent is added, the copper will not be completely precipitated, and the result will be too low. But, if the directions given are closely followed, and care is taken, this method yields very accurate results.

If the precipitate is free from impurity, it may be ignited at the highest temperature obtainable with a Bunsen burner, without changing; but, if ignited in the presence of carbonaceous matter, or of reducing gases, it is reduced quite rapidly. For this reason, a drop of concentrate nitric acid is always added to the filter ash, to change any copper that has been reduced by the burning paper back to cupric oxide, and a cover is always placed on the crucible before ignition, to protect the precipitate from reducing gases. If the final result is too low, it is always best to add a drop of concentrate nitric acid to the precipitate, and again ignite and weigh it, after heating carefully to drive off the excess of nitric acid. If this second weight is higher than the first, it shows that the precipitate was partly reduced, and the second weight should be accepted as correct.

When heated to a very high temperature, the precipitate gradually loses oxygen and is partly reduced to the cuprous condition; hence, it should always be ignited over a Bunsen burner, rather than a blast lamp. If allowed to stand in the air, it gradually absorbs moisture and thus increases in weight; hence, it should always be allowed to cool in a desiccator before weighing.

Many organic compounds prevent the complete precipitation of copper as oxide; hence, after testing the filtrate with a few drops of the reagent used, if this produces no precipitate, and it is possible that organic matter may be present, it should always be tested with hydrogen sulphide after acidulating with hydrochloric acid. If this should produce a precipitate, more of the reagent is added until precipitation is complete. Filter and wash the precipitate, dissolve it in a little nitric acid, filter, precipitate the copper from the filtrate, filter, and ignite with the main precipitate after washing and drying it. Or, better still, when organic matter is suspected, employ the following method.

18. Determination of Copper as Sulphide.—Weigh about 1 gram of pure dry copper-sulphate crystals $CuSO_4, 5H_2O$ on a watch glass, transfer them to a beaker, and dissolve in about 100 cubic centimeters of hot water and 1 cubic centimeter of concentrate hydrochloric acid. Heat the solution to boiling, and, while keeping its temperature as near as possible to the boiling point, conduct through it a current of hydrogen sulphide, which has been generated in a Kipp generator and washed in water, until the copper is completely precipitated as black copper sulphide CuS. The operation is complete when hydrogen sulphide no longer produces a precipitate in the clear, colorless liquid above the precipitate. As soon as the precipitate settles, filter as rapidly as possible, and with the least possible exposure of the precipitate to the air. Wash the precipitate on the filter with water containing a little hydrogen sulphide, and dry it in the air bath with as little delay as possible. Transfer the dry precipitate to a watch glass, burn the filter in a Rose crucible,* which has previously been ignited and weighed, and when this has cooled, add the precipitate from the watch

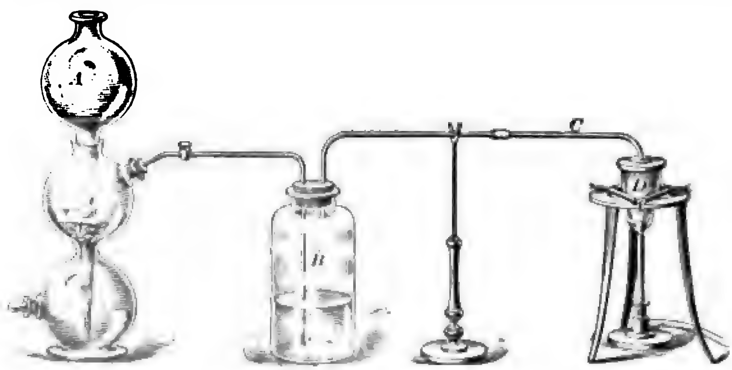

Fig. 6.

glass. Cover the precipitate with about .5 gram of powdered sulphur, cover the crucible, and lead in hydrogen through a porcelain tube, which just reaches through the

* A Rose crucible is a deep, narrow, porcelain crucible having a perforated cover.

perforation in the crucible cover, as shown in Fig. 6. *A* is a Kipp generator, in which hydrogen is prepared by the action of dilute sulphuric acid on zinc; *B* contains concentrate sulphuric acid, in which the hydrogen is washed; *C* is a porcelain tube, which conducts the hydrogen to the crucible *D*. The flow of hydrogen should be so regulated that it passes through the wash bottle *B* at the rate of 2 or 3 bubbles per second. After the hydrogen has been running until the air has all been expelled from the apparatus, so that the crucible contains an atmosphere of pure hydrogen, place a Bunsen burner under it and heat, gently at first, but gradually increasing the heat, and finally igniting for 10 minutes at the highest temperature obtainable with a blast lamp. Remove the burners and allow the crucible and precipitate to cool while the hydrogen is passing through it. As soon as it is cool, remove it to the balance and weigh it; or, just before it is quite cold, it may be removed to a desiccator, allowed to become quite cold, and weighed. The high ignition in a current of hydrogen reduces cupric sulphide CuS to cuprous sulphide Cu_2S; hence, the weight obtained minus the weight of the empty crucible is the weight of cuprous sulphide Cu_2S. This weight multiplied by 79.82, and the product divided by the weight of sample taken, gives the percentage of copper in the sample. The proportion used to calculate the weight of copper is

$$Cu_2S : Cu_2 = \text{wt. of } Cu_2S : x.$$

19. Notes and Precautions.—This method has a number of advantages and is preferred to the other methods by many chemists. Copper sulphide is almost absolutely insoluble in water and very dilute hydrochloric acid, and its formation is not prevented by the presence of organic compounds; it does not adhere to the vessel in which it is precipitated; it collects and settles more quickly, and is filtered more rapidly than copper oxide. As no fixed compounds are introduced as reagents, it requires less washing, and if proper care is taken, this method yields very accurate results. On the other hand, the method requires great care. The

precipitate must be shielded from the air as much as possible, since the air oxidizes it to soluble copper sulphate. For this reason, the determination should always be carried through as rapidly as possible. In washing the precipitate on the filter, as soon as one lot of wash water runs through, another lot should be added, in order to keep the precipitate from the air, and the wash water should always contain some pure hydrogen sulphide.

In igniting the precipitate, great care must be taken to run the hydrogen until all the air is out of the apparatus before bringing the burner under the crucible. If the generator contains air when the light is applied, it will cause an extremely violent explosion, which may do much damage; and if the air has been expelled from the generator, but some remains in the crucible, an explosion will be caused in the crucible, which is likely to break it, or at least to cause a loss of precipitate. In order to test the hydrogen for air, hold a test tube, mouth down, over the tube through which the hydrogen is passing until it is thoroughly filled, remove it from the jet, and, without allowing it to diffuse with the air, apply a light to the mouth of the tube. If no explosion results, we may assume that the air is all out of the generator; and after connecting the apparatus and running the hydrogen through the crucible for several minutes, the air will all be expelled and the Bunsen flame may be applied. The precipitate must be heated gently at first, and the heat gradually increased until the highest power of the blast lamp is reached.

In case a Rose crucible and a porcelain tube to lead the hydrogen through are not at hand, a common porcelain crucible and an ordinary clay pipe may be made to serve the purpose. The bowl of the pipe is fitted either over or into the top of the crucible as closely as possible, and the stem is attached to the tube leading the hydrogen from the wash bottle.

20. Determination of Copper by Electrolysis.—Weigh out about 1 gram of copper sulphate, transfer it to a

beaker of rather deep form, and dissolve it in about 100 cubic centimeters of water and from 5 to 10 cubic centimeters of dilute nitric acid. Connect the zinc of an ordinary crow-foot gravity cell *A*, Fig. 7, with a weighed electrode made by soldering a piece of platinum foil to a platinum wire, as

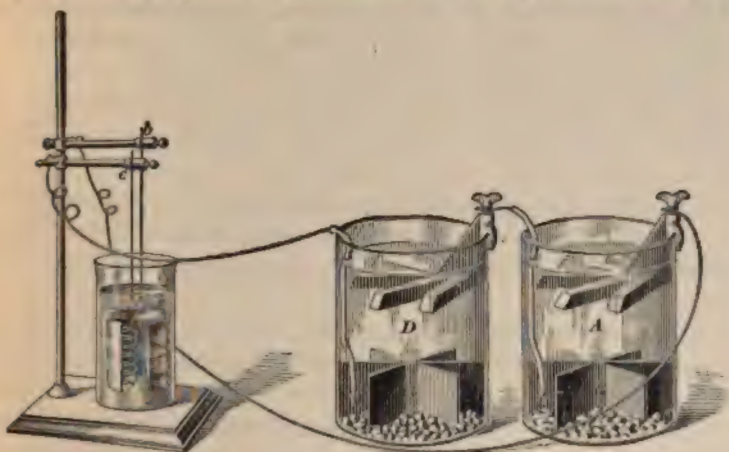

FIG. 7.

shown at *b*, and suspend this negative electrode in the solution of copper sulphate, so that it does not touch the side or bottom of the beaker. A rather stout platinum wire *c* bent in the form of a spiral, serves well for a positive electrode. It is attached to the wire leading from the copper of a second cell *D* connected with *A* by means of a binding screw, forming a battery, and must be suspended in the solution so that it does not come in contact with the negative electrode at any point. Add water until the solution covers the foil of the negative electrode and allow the solution to stand for 4 or 6 hours. The electric current passing through the solution decomposes the copper sulphate and deposits the copper on the negative electrode. When the solution becomes colorless, remove a drop of it on a glass rod, and bring it in contact with a drop of potassium ferrocyanide, or hydrogen sulphide, on a porcelain plate. If no coloration is produced, the copper is all deposited. Have in readiness four beakers of

hot water, a beaker of alcohol, and an air bath heated to 100°. Remove the negative electrode from the liquid without disconnecting, or siphon off the liquid in order to avoid breaking the current, until the electrode is out of the liquid. Quickly plunge the negative electrode, containing the copper, into the first beaker of water, then remove it to the second, third, etc., and finally wash in the alcohol. Transfer it quickly from the alcohol to the air bath, and allow it to stand there on a watch glass until dry. As soon as dry, allow it to cool in a desiccator, and weigh as soon as cool. This weight minus the weight of the electrode is equal to the weight of copper, which weight divided by the weight of copper sulphate taken for analysis and this result multiplied by 100, gives the percentage of copper in the sample.

21. Notes and Precautions.—This is an extremely accurate method of determining copper, and each student should make at least one determination by this method if possible. In case a platinum negative electrode such as described is not available, quite accurate results may be obtained by using a thin, perfectly clean piece of copper, attached to a platinum wire for a negative electrode. When determining copper in pure copper sulphate, but few precautions are necessary. The electric current should not be broken until the negative electrode is taken out of the liquid, for if left in the liquid after the current is broken, the acid solution will at once begin to dissolve the copper from the electrode. The washing, drying, etc. should always be carried out as rapidly as possible, as the copper is oxidized in the air. The strength of the current is an important matter. The current from an ordinary gravity cell, when working well, can usually be made to answer the purpose. It is usually better, however, to connect two cells, as shown in Fig. 7, but too strong a current must be avoided, or the copper will be deposited in a loose, spongy mass, which does not adhere firmly to the electrode, and which oxidizes rapidly in the air. Some chemists use a solution containing only sulphates and a little free sulphuric acid for electrolysis; but with such a

solution, more or less arsenic or antimony, if present even in small quantities, will be deposited with the copper, giving the deposit a dark color. Nitric acid, even in very small amount, largely prevents such deposits, and gives a clean, bright surface to the precipitate, but it does not entirely prevent the precipitation of bismuth if present; and if the solution contains nickel and zinc, they will begin to deposit as soon as all the copper is down. When nitric acid is present, it is also necessary to use greater care in disconnecting the electrodes, as the nitric acid attacks the copper very rapidly as soon as the current is interrupted.

Hydrochloric acid, chlorides, and organic acids are not admissible in solutions from which copper is to be deposited quantitatively by electrolysis. If an air bath is not at hand, the electrode may be placed on a watch glass and heated over a Bunsen burner, until the alcohol is dried off of it, but care must be taken in doing this not to heat the electrodes too strongly.

In many cases this method is much handier than the others, and yields extremely accurate results. On account of its advantages, it has been so largely adopted in this country that it is frequently spoken of as the "United States method."

NICKEL.

22. Determination of Nickel as Oxide.—Weigh up 1 gram or a trifle more of nickel-ammonium sulphate $Ni(NH_4)_2 2SO_4, 6H_2O$, which has been dried in a desiccator if necessary, and dissolve it in a porcelain dish in about 150 cubic centimeters of water. Heat the solution to boiling, precipitate the nickel with an excess of sodium hydrate, and continue the boiling until the odor of ammonia has disappeared. Then add bromine water in small, successive quantities, with constant stirring, until the precipitate is completely black and of a uniform texture. Care must be taken to keep the solution slightly alkaline all the time during this operation. Allow the precipitate to subside,

decant the clear liquid through a filter, and wash three or four times by decantation with hot water, bringing to boiling after each addition of water, and allowing the precipitate to settle before decanting. Then bring the precipitate on to the filter, and wash with hot water until a test of the washings does not give an alkaline reaction with litmus paper. Dry the precipitate, remove it to a watch glass, burn the filter in a weighed crucible, add a drop of nitric acid to the residue, evaporate this to dryness, add the main precipitate, ignite strongly, cool in a desiccator, and weigh as nickel oxide NiO, which contains 78.66 per cent. of nickel, if we take $Ni = 59$, and $O = 16$. The proportion for calculating the weight of nickel is

$$NiO : Ni = \text{wt. of } NiO : x.$$

Instead of weighing as oxide, we may burn the filter in a weighed Rose crucible, add the main precipitate, lead in a current of pure hydrogen, ignite in the hydrogen, as in the case of copper sulphide, and weigh as metallic nickel. This method gives very good results, and is useful in checking the results obtained by weighing the nickel as oxide. It was largely used at one time, but at present it seems to have fallen into disuse.

23. Notes and Precautions.—Enough sodium hydrate should be added to completely precipitate the nickel and still have enough left in the solution to keep it alkaline when the bromine water is added, but a large excess should be avoided, as it is more difficult to wash it out of the precipitate if a large excess is present. The precipitate is soluble in ammonia or ammonium salts, but is reprecipitated by sodium hydrate after the ammonia has been expelled by the sodium hydrate. For this reason, the boiling should always be continued until all the ammonia is expelled before adding the bromine water. The precipitate at first formed, when sodium hydrate is added to the nickel solution, is apple-green nickel hydrate $Ni(OH)_2$. This is oxidized to $Ni(OH)_3$ by the bromine water, and this in turn is changed to NiO when highly heated. The precipitate carries down some of the

reagent with it, and this can only be completely removed by very thorough washing with hot water. The oxide is not changed by heating in the air, unless a reducing agent, such as carbonaceous matter or reducing gases, is present, but it is readily reduced to metallic nickel if ignited in an atmosphere of hydrogen.

24. Determination of Nickel by Electrolysis.—Dissolve about 1 gram of nickel-ammonium sulphate in about 100 cubic centimeters of water in a beaker of rather deep form. Make the solution strongly alkaline with ammonia and pass an electric current through it, exactly as in the case of copper, until the solution is colorless, and a drop of it, when removed to a white plate on a glass rod and mixed with a drop of ammonium sulphide, gives no coloration. Disconnect the negative electrode, wash in hot water and alcohol, as in the case of copper, dry, and weigh quickly. This weight minus the weight of the electrode gives the weight of the nickel, which weight divided by the weight of the sample taken and this result multiplied by 100, gives the per cent. of nickel in the sample.

25. Notes and Precautions.—For practice, the same electric current that was used for copper may be used for nickel, but if many nickel determinations are to be made by this method, a stronger current should be used. The current furnished by a battery of three cells is usually recommended. As the nickel is deposited, the action of the current grows slower, and the thicker the coating of nickel, the slower it becomes, so that with a rather weak current, the last traces of nickel are deposited only after long treatment. This peculiarity is particularly marked with cold solutions, and it is now generally recommended to heat the solution to 60° or 70° while passing the electric current through it. If the solution is thus heated, ammonia must be added from time to time to take the place of that driven off by the heat. The washing, drying, and weighing should be performed as quickly as possible, as in the case of copper. The nickel may

precipitate has settled, decant the clear liquid through a filter. Add hot water and a few drops of dilute nitric acid to the precipitate, heat nearly to boiling, allow the precipitate to settle, filter, using the paper through which the clear liquid was decanted, and wash thoroughly with hot water. Dry the precipitate thoroughly, remove it as completely as possible to a watch glass, and burn the filter in a weighed porcelain crucible. After the crucible has become cool, add 2 or 3 drops of nitric acid to the filter ash, and heat gently to dissolve any particles of metallic silver that may have been reduced by the burning paper. Then add 2 drops of concentrate hydrochloric acid, heat gently to drive off the excess of acid, and ignite the residue very gently. After the crucible has become cool, add the main precipitate, and heat gently with the cover on the crucible until the precipitate just begins to fuse around the edges. Remove the burner, cool in a desiccator, weigh as silver chloride, and calculate the percentage of silver. The percentage of silver in silver chloride is generally given as 75.27. The proportion for the calculation of the weight of silver is

$$AgCl : Ag = \text{wt. of } AgCl : x.$$

31. Notes and Precautions.—Arts. **12** and **13** should be read in connection with this determination. The precipitate is the same as the one obtained in the determination of chlorine and should be treated in a similar manner. The determination of chlorine, however, is rather easier than the determination of silver, as the precipitate collects and settles much more readily in the presence of silver nitrate than in the presence of hydrochloric acid. This difficulty is largely overcome, however, by having a little free nitric acid present and by continued stirring. A large amount of nitric acid should be avoided, and a large excess of hydrochloric acid should not be added, as either of these acids, when present in considerable quantity, dissolve more or less of the precipitate. The same care must be taken to protect the precipitate from the light that was necessary in the determination of chlorine, but the silver may be precipitated from a much

warmer solution than the chlorine, as there is no danger of loss by volatilization at this point. Care must be exercised in igniting the precipitate, however, as silver chloride volatilizes easily and is reduced by a strong heat.

32. Determination of Silver as Sulphide or as Metallic Silver.—Dissolve about .5 gram of pure dry silver nitrate in about 150 cubic centimeters of water, to which from 3 to 5 cubic centimeters of dilute nitric acid are added, and through this solution lead a current of pure, washed hydrogen sulphide, until the silver is completely precipitated as black silver sulphide. Filter as quickly as possible and wash with hot water on a filter which has been dried and weighed as directed in Art. 27. Dry the filter and precipitate in an air bath at 105°, until a constant weight is obtained, and weigh between matched watch glasses. If the work is properly done, the precipitate will be Ag_2S, which contains 87.09 per cent. of silver. The proportion for calculating the weight of silver is

$$Ag_2S : Ag_2 = \text{wt. of } Ag_2S : x.$$

Unless great care is taken in this determination, the precipitate is likely to contain free sulphur, thus yielding too high a result. For this reason, unless the operator is certain that the precipitate does not contain free sulphur, it is best to treat it as follows: After washing on the filter with hot water, dry the precipitate as usual, remove it as completely as possible to a watch glass, and burn the filter in a weighed Rose crucible. When the crucible has become cool, add the precipitate, cover the crucible, lead in hydrogen, and ignite over the Bunsen burner at a moderate temperature for 15 minutes. Remove the burner, but continue the current of hydrogen until the crucible and precipitate are cool, and weigh at once. Then lead in hydrogen, ignite again for 5 minutes, cool in a current of hydrogen, and weigh again. If the second weight is less than the first, the ignition in hydrogen must be repeated until a constant weight is obtained. The precipitate is now metallic silver, and the weight of it divided by the weight of the sample taken and

this multiplied by 100, gives the percentage of silver in the sample. If the silver is weighed as sulphide, it is a good plan, after weighing, to reduce it to metallic silver as just described, and weigh again. This gives a good check on the work.

33. Notes and Precautions.—The solution from which the silver is precipitated as sulphide should contain a little nitric or sulphuric acid (preferably nitric) or the precipitate will not collect and settle rapidly; but a large amount of free acid must be avoided, as it is likely to decompose the hydrogen sulphide, setting free some of the sulphur, which would give too high a result if the silver were weighed as sulphide. The precipitate is almost absolutely insoluble in water and very dilute acids, but dissolves to a greater or less extent in stronger acids. As a solution of hydrogen sulphide is decomposed by the action of the air, the solution should be protected from the air as much as possible during precipitation. This is best accomplished by covering the beaker with a watch glass having a perforation in the center, and passing the tube which conducts the hydrogen sulphide into the solution through this perforation. Then, by leading a rather rapid current of hydrogen sulphide (5 or 6 bubbles per second) through the solution, the air will be expelled from the top of the beaker, and the surface of the liquid will be protected by the hydrogen-sulphide gas that fills the upper part of the beaker. Filtration should be accomplished as rapidly as possible, to avoid exposure to the air, and the precipitate should be washed without delay. If the silver is to be weighed as sulphide, the method of weighing described in Art. 27 should be used. If it is weighed as metallic silver, the method of ignition described in Art. 18 should be followed and the precautions mentioned in Art. 19 should be observed. Free sulphur is not added in this case, as the object of the ignition is to expel the sulphur, and the precipitate must not be heated over the blast lamp, but only at a moderate temperature over the Bunsen burner. These methods, when properly executed, give accurate results, but

as such great care is required in determining silver as sulphide, and as the method of weighing it as metallic silver is rather long and troublesome at best, the determination as chloride is used much more largely than either of these.

MAGNESIUM.

34. Determination of Magnesium as Pyrophosphate.—Dissolve 1 gram, or a trifle more, of magnesium-ammonium sulphate $Mg(NH_4)_2 2SO_4, 6H_2O$ in about 100 cubic centimeters of water, add from 5 to 10 drops of hydrochloric acid, 5 cubic centimeters of ammonium chloride, and then ammonium hydrate in slight excess. If this produces a precipitate, dissolve it in a little hydrochloric acid and again render the solution slightly alkaline with ammonia. Should a precipitate again separate, it shows that the solution does not contain a sufficient quantity of ammonium chloride to prevent the precipitation of magnesium hydrate, and solution in hydrochloric acid and subsequent treatment with ammonia must be continued until a clear alkaline solution is obtained. Then add a solution of sodium-ammonium phosphate (microcosmic salt) in small successive portions until the solution contains a moderate excess of the precipitant, stirring the solution after each addition of a few drops of the reagent, until the precipitate, which is white and flocculent at first, assumes a silky, crystalline appearance, but taking care not to let the stirring rod strike the side or bottom of the beaker. After all the magnesium is precipitated and a moderate excess of the reagent has been added, add 25 cubic centimeters of concentrate ammonia, and stand the beaker and contents in a cool place for 5 or 6 hours, for the precipitate to collect and settle. Filter and wash thoroughly, but not too long, on the filter, with a solution containing 1 part of concentrate ammonia and 4 parts of water. The washing is complete when silver nitrate fails to produce a precipitate, or produces only a slight opalescence, in a small test of the washings, after acidulating

with nitric acid. Dry the precipitate thoroughly, remove it as completely as possible to a watch glass, and burn the filter in a weighed porcelain crucible. When the crucible becomes cool, add the precipitate and heat gently over the Bunsen burner at first, but gradually raise the temperature, and finally heat to full redness for 10 minutes, cool in a desiccator, and weigh. If the precipitate is not quite white, add a few drops of concentrate nitric acid, evaporate the acid at a gentle heat, and then raise the temperature to bright redness for 5 minutes. Cool in a desiccator and weigh as magnesium pyrophosphate $Mg_2P_2O_7$, which contains 21.62 per cent. of magnesium. The weight of magnesium may be calculated by the proportion

$$Mg_2P_2O_7 : Mg_2 = \text{wt. of } Mg_2P_2O_7 : x.$$

35. Notes and Precautions.—Magnesium-ammonium phosphate is slightly soluble in pure water, but is much less soluble in a dilute solution of ammonia; hence, ammonia should always be added after adding the reagent, and the precipitate should always be washed with water containing ammonia. The precipitate dissolves more readily in water containing ammonium chloride than in water containing only ammonium hydrate, but ammonium chloride should be present to prevent precipitation of magnesium as hydrate. The precipitate separates more rapidly and completely in the cold than when heated; hence, precipitation and filtration should be performed in the cold, and the precipitate should be washed with a cold solution. Stirring also promotes the formation of the precipitate, and the solution should be thoroughly stirred while the precipitant is added, in order to secure a crystalline precipitate, but care must be taken not to allow the stirring rod to touch the side or bottom of the beaker, or it will break some of the crystals on the glass, leaving particles of the precipitate adhering so tenaciously to the glass as to make it very difficult to remove them. When ignited, the magnesium ammonium phosphate is changed to magnesium pyrophosphate. An experienced chemist may ignite the precipitate in a platinum crucible

rithout danger, if he is careful, but it is better to use a porcein crucible, for when this precipitate is ignited in platium in the presence of the carbon of the filter paper, the hosphorus tends to unite with the platinum, forming platium phosphide and rendering the crucible brittle. The recipitate is usually ignited over a blast lamp, but in the bsence of a blast lamp, a Bunsen burner may be made to erve the purpose. In this case, however, the precipitate hould be heated at the highest temperature obtainable for .t least 15 minutes, and a constant weight must be obtained.

MANGANESE.

36. Determination of Manganese as Pyrophosphate. Dissolve about 1 gram of manganese-ammonium sulphate $Mn(NH_4)_2 2SO_4, 6H_2O$ in 100 cubic centimeters of water and precipitate the manganese as manganese-ammonium phosphate by adding a solution of sodium-ammonium phosphate, using at least double the quantity of the reagent required to unite with the manganese. Dissolve the precipitate in a slight excess of hydrochloric acid, heat the solution to boiling, and reprecipitate the manganese-ammonium phosphate by adding ammonium hydrate, a few drops at a time, and stirring after each addition, until the precipitate, which is white and curdy at first, assumes a silky crystalline appearance. When the manganese is completely precipitated and the precipitate has become crystalline, add 5 cubic centimeters of dilute ammonia, stir well, stand in a warm place for half an hour, and then stand in a cold place for 1 or 2 hours, until the precipitate collects and settles. When the precipitate has completely settled, and the liquid has become cold, filter and wash on the filter with a solution containing 5 cubic centimeters of dilute ammonia and 5 grams of ammonium nitrate in 100 cubic centimeters of water. The precipitate should be thoroughly, but not excessively, washed. Dry the precipitate thoroughly, remove it as completely as possible to a watch glass, and burn the filter in a weighed porcelain crucible. When the crucible becomes cool, add the

with nitric acid. Dry the precipitate thoroughly, remove it as completely as possible to a watch glass, and burn the filter in a weighed porcelain crucible. When the crucible becomes cool, add the precipitate and heat gently over the Bunsen burner at first, but gradually raise the temperature, and finally heat to full redness for 10 minutes, cool in a desiccator, and weigh. If the precipitate is not quite white, add a few drops of concentrate nitric acid, evaporate the acid at a gentle heat, and then raise the temperature to bright redness for 5 minutes. Cool in a desiccator and weigh as magnesium pyrophosphate $Mg_2P_2O_7$, which contains 21.62 per cent. of magnesium. The weight of magnesium may be calculated by the proportion

$$Mg_2P_2O_7 : Mg_2 = \text{wt. of } Mg_2P_2O_7 : x.$$

35. Notes and Precautions.—Magnesium-ammonium phosphate is slightly soluble in pure water, but is much less soluble in a dilute solution of ammonia; hence, ammonia should always be added after adding the reagent, and the precipitate should always be washed with water containing ammonia. The precipitate dissolves more readily in water containing ammonium chloride than in water containing only ammonium hydrate, but ammonium chloride should be present to prevent precipitation of magnesium as hydrate. The precipitate separates more rapidly and completely in the cold than when heated; hence, precipitation and filtration should be performed in the cold, and the precipitate should be washed with a cold solution. Stirring also promotes the formation of the precipitate, and the solution should be thoroughly stirred while the precipitant is added, in order to secure a crystalline precipitate, but care must be taken not to allow the stirring rod to touch the side or bottom of the beaker, or it will break some of the crystals on the glass, leaving particles of the precipitate adhering so tenaciously to the glass as to make it very difficult to remove them. When ignited, the magnesium ammonium phosphate is changed to magnesium pyrophosphate. An experienced chemist may ignite the precipitate in a platinum crucible

without danger, if he is careful, but it is better to use a porcelain crucible, for when this precipitate is ignited in platinum in the presence of the carbon of the filter paper, the phosphorus tends to unite with the platinum, forming platinum phosphide and rendering the crucible brittle. The precipitate is usually ignited over a blast lamp, but in the absence of a blast lamp, a Bunsen burner may be made to serve the purpose. In this case, however, the precipitate should be heated at the highest temperature obtainable for at least 15 minutes, and a constant weight must be obtained.

MANGANESE.

36. Determination of Manganese as Pyrophosphate. Dissolve about 1 gram of manganese-ammonium sulphate $Mn(NH_4)_2 2SO_4, 6H_2O$ in 100 cubic centimeters of water and precipitate the manganese as manganese-ammonium phosphate by adding a solution of sodium-ammonium phosphate, using at least double the quantity of the reagent required to unite with the manganese. Dissolve the precipitate in a slight excess of hydrochloric acid, heat the solution to boiling, and reprecipitate the manganese-ammonium phosphate by adding ammonium hydrate, a few drops at a time, and stirring after each addition, until the precipitate, which is white and curdy at first, assumes a silky crystalline appearance. When the manganese is completely precipitated and the precipitate has become crystalline, add 5 cubic centimeters of dilute ammonia, stir well, stand in a warm place for half an hour, and then stand in a cold place for 1 or 2 hours, until the precipitate collects and settles. When the precipitate has completely settled, and the liquid has become cold, filter and wash on the filter with a solution containing 5 cubic centimeters of dilute ammonia and 5 grams of ammonium nitrate in 100 cubic centimeters of water. The precipitate should be thoroughly, but not excessively, washed. Dry the precipitate thoroughly, remove it as completely as possible to a watch glass, and burn the filter in a weighed porcelain crucible. When the crucible becomes cool, add the

precipitate and again ignite, gently at first, but finally at bright redness, until a constant weight is obtained. Ten minutes' ignition at the full power of the blast lamp will be sufficient. Allow the crucible and contents to cool in a desiccator, and weigh as manganese pyrophosphate $Mn_2P_2O_7$, which contains 38.73 per cent. of manganese. The weight of manganese may be calculated by the proportion

$$Mn_2P_2O_7 : Mn_2 = \text{wt. of } Mn_2P_2O_7 : x.$$

37. Notes and Precautions.—Manganese-ammonium phosphate is very slightly soluble in hot water, but less soluble in cold water. A small amount of ammonia in water appears to diminish its solubility, but it dissolves quite perceptibly in a large amount of ammonia. A moderate amount of ammonium nitrate does not seem to affect the solubility of the precipitate, but is added to furnish oxygen to help burn the filter paper, which is often very difficult to burn in this case unless an oxidizing agent is present. As ammonium nitrate is easily decomposed and volatilized by heat, its presence can do no harm. The precipitate should always be obtained in the crystalline form, and this is best accomplished by precipitating slowly and stirring well, as directed above; but the crystalline precipitate may also be obtained by adding an excess of ammonia at once and continuing the boiling for 15 or 20 minutes, while the mixture is stirred continuously. The solution has a great tendency to bump when treated this way, even if stirred without interruption. If the bumping is so violent that there is danger of loss, the liquid must be heated nearly to the boiling point (preferably on a water bath) for 2 or 3 hours and stirred frequently. When using this method, care must be taken to keep the solution alkaline all the time. The ammonia will be driven off by the heat, and a few drops of dilute ammonia must be added from time to time, taking care not to add a large excess. In the presence of a large excess of ammonia or ammonium compounds, the precipitate dissolves to a considerable extent if only a slight excess of the reagent is present, but this is largely overcome by adding a large excess of the reagent.

The precipitate seems most insoluble when from two to three times the quantity of reagent required by calculation is present.

When ignited, the manganese-ammonium phosphate $MnNH_4PO_4$ is changed to manganese pyrophosphate $Mn_2P_2O_7$. If ignited too strongly at first, the escaping gases are liable to carry particles of the precipitate with them; hence, the precipitate should be ignited gently at first and the temperature gradually raised to full redness. The precipitate is generally ignited over the blast lamp, but continued ignition at the highest temperature obtainable with a good Bunsen burner serves to convert the precipitate into pyrophosphate.

CALCIUM.

38. Determination of Calcium as Oxide.—Weigh out about .5 gram of pulverized calcium carbonate that has been dried in an air bath and cooled in a desiccator, transfer it to a beaker of rather deep form, and cover the beaker with a watch glass. Draw the watch glass slightly to one side and add dilute hydrochloric acid, a little at a time, until the sample is dissolved, avoiding a large excess of acid, and placing the watch glass back over the beaker after each addition of acid, to prevent loss by spattering. Add about 100 cubic centimeters of water, heat to boiling, add 10 cubic centimeters of ammonia, and precipitate the calcium with a moderate excess of ammonium oxalate. Continue the boiling, with constant stirring, for a minute or two. Then stand the beaker in a warm place for at least 4 hours, and longer if necessary, for the precipitate to collect and settle perfectly, leaving the supernatant liquid clear. Decant the clear liquid through a filter, leaving the precipitate in the beaker. Add about 100 cubic centimeters of hot water and a few cubic centimeters of dilute ammonia, stir well, and stand in a warm place until it settles again. Now filter and wash well on the filter with hot water containing 1 or 2 cubic centimeters of concentrate ammonia in 100 cubic

precipitate and again ignite, gently at first, but finally at bright redness, until a constant weight is obtained. Ten minutes' ignition at the full power of the blast lamp will be sufficient. Allow the crucible and contents to cool in a desiccator, and weigh as manganese pyrophosphate $Mn_2P_2O_7$, which contains 38.73 per cent. of manganese. The weight of manganese may be calculated by the proportion

$$Mn_2P_2O_7 : Mn_2 = \text{wt. of } Mn_2P_2O_7 : x.$$

37. Notes and Precautions.—Manganese-ammonium phosphate is very slightly soluble in hot water, but less soluble in cold water. A small amount of ammonia in water appears to diminish its solubility, but it dissolves quite perceptibly in a large amount of ammonia. A moderate amount of ammonium nitrate does not seem to affect the solubility of the precipitate, but is added to furnish oxygen to help burn the filter paper, which is often very difficult to burn in this case unless an oxidizing agent is present. As ammonium nitrate is easily decomposed and volatilized by heat, its presence can do no harm. The precipitate should always be obtained in the crystalline form, and this is best accomplished by precipitating slowly and stirring well, as directed above; but the crystalline precipitate may also be obtained by adding an excess of ammonia at once and continuing the boiling for 15 or 20 minutes, while the mixture is stirred continuously. The solution has a great tendency to bump when treated this way, even if stirred without interruption. If the bumping is so violent that there is danger of loss, the liquid must be heated nearly to the boiling point (preferably on a water bath) for 2 or 3 hours and stirred frequently. When using this method, care must be taken to keep the solution alkaline all the time. The ammonia will be driven off by the heat, and a few drops of dilute ammonia must be added from time to time, taking care not to add a large excess. In the presence of a large excess of ammonia or ammonium compounds, the precipitate dissolves to a considerable extent if only a slight excess of the reagent is present, but this is largely overcome by adding a large excess of the reagent.

The precipitate seems most insoluble when from two to three times the quantity of reagent required by calculation is present.

When ignited, the manganese-ammonium phosphate $MnNH_4PO_4$ is changed to manganese pyrophosphate $Mn_2P_2O_7$. If ignited too strongly at first, the escaping gases are liable to carry particles of the precipitate with them; hence, the precipitate should be ignited gently at first and the temperature gradually raised to full redness. The precipitate is generally ignited over the blast lamp, but continued ignition at the highest temperature obtainable with a good Bunsen burner serves to convert the precipitate into pyrophosphate.

CALCIUM.

38. Determination of Calcium as Oxide.—Weigh out about .5 gram of pulverized calcium carbonate that has been dried in an air bath and cooled in a desiccator, transfer it to a beaker of rather deep form, and cover the beaker with a watch glass. Draw the watch glass slightly to one side and add dilute hydrochloric acid, a little at a time, until the sample is dissolved, avoiding a large excess of acid, and placing the watch glass back over the beaker after each addition of acid, to prevent loss by spattering. Add about 100 cubic centimeters of water, heat to boiling, add 10 cubic centimeters of ammonia, and precipitate the calcium with a moderate excess of ammonium oxalate. Continue the boiling, with constant stirring, for a minute or two. Then stand the beaker in a warm place for at least 4 hours, and longer if necessary, for the precipitate to collect and settle perfectly, leaving the supernatant liquid clear. Decant the clear liquid through a filter, leaving the precipitate in the beaker. Add about 100 cubic centimeters of hot water and a few cubic centimeters of dilute ammonia, stir well, and stand in a warm place until it settles again. Now filter and wash well on the filter with hot water containing 1 or 2 cubic centimeters of concentrate ammonia in 100 cubic

centimeters. Dry the precipitate, remove it as completely as possible to a watch glass, and burn the filter in a weighed platinum crucible. Add the precipitate and again ignite, gently at first, but gradually raise the temperature, and finally heat for 20 minutes at the highest power of the blast lamp. Allow the crucible and contents to cool in a desiccator and weigh without delay. Then moisten the precipitate with a drop or two of water, heat gently to evaporate the water, and then ignite for 5 or 10 minutes at the highest temperature obtainable with a blast lamp. Cool in a desiccator, and weigh as soon as cool. This weight should be the same as the first. If the precipitate has lost weight during the ignition, it must be reignited until a constant weight is obtained. The precipitate is now CaO, which contains 71.43 per cent. of calcium. The weight of calcium may be calculated by the proportion

$$CaO : Ca = \text{wt. of } CaO : x.$$

39. Notes and Precautions.—Calcium oxalate CaC_2O_4 is a white crystalline powder, which is almost absolutely insoluble in water or dilute solutions of the alkalies, but is very soluble in acids. Even oxalic and acetic acids dissolve considerable quantities of it. The precipitate separates most rapidly and completely from a hot solution containing a decided excess of ammonia; hence, such a solution is nearly always employed, and the wash water is generally made slightly ammoniacal to prevent the possibility of a free acid coming in contact with the precipitate, but if the water is absolutely free from acid, this is unnecessary, as the calcium oxalate is so nearly insoluble in pure water.

When calcium oxalate is ignited, it gives off carbon monoxide at a dull-red heat, forming calcium carbonate; at a little higher temperature, carbon dioxide begins to escape, and calcium oxide is formed, but all the carbon dioxide is expelled only by continued intense ignition. The calcium oxide obtained by ignition should be quickly weighed as soon as cool, for it absorbs moisture and carbon dioxide from the air if allowed to stand. This absorption is not rapid enough

to interfere with the weighing, if it is done promptly. This method yields very accurate results.

40. Determination of Calcium as Sulphate.—Precipitate the calcium as oxalate and dry the precipitate as directed in Art. **38.** Remove the precipitate as completely as possible to a watch glass, burn the filter in a porcelain crucible, and, after cooling, add the precipitate. Now add concentrate sulphuric acid to the precipitate, drop by drop, until it is thoroughly moistened, but avoid much excess of acid. Heat the crucible cautiously, until the swelling of the mass subsides and white fumes of SO_3 cease to be driven off. Then raise the temperature and heat the crucible to a cherry red for 5 minutes over the Bunsen burner. Cool in a desiccator and weigh as calcium sulphate $CaSO_4$, which contains 29.41 per cent. of calcium.

41. Notes and Precautions.—The determination of calcium as oxide is preferable to the sulphate method whenever it can be employed, as it is simpler and there is not so much danger of error; but if a blast lamp is not available, the oxide method cannot be used, and it is difficult to obtain heat enough to change the oxalate to oxide in a porcelain crucible, even with a blast lamp. In the absence of a blast lamp and a platinum crucible, the sulphate method may be used, and if properly executed, will yield accurate results; but great care should be exercised when using it. When the precipitate is heated with sulphuric acid, it swells up and particles are liable to be lost if great care is not taken. There is also danger of loss of precipitate when evaporating the excess of sulphuric acid. The best way to do this is to hold the burner in the hand and allow the flame to strike the crucible (which should always be covered during this operation) only near the top until most of the excess of acid is expelled; then gradually heat the lower part of the crucible also, and slowly raise the temperature until the crucible becomes quite red. Calcium sulphate should never be ignited over the blast lamp, as it is partly reduced to sulphide by strong ignition.

BARIUM.

42. Determination of Barium as Sulphate.—Dissolve from .6 to 1 gram of barium chloride $BaCl_2 2H_2O$ in 100 to 150 cubic centimeters of water, add 1 cubic centimeter of dilute hydrochloric acid and 5 cubic centimeters of ammonium chloride, and heat the solution to boiling. Then precipitate the barium as sulphate by adding dilute sulphuric acid, drop by drop, while the solution is being stirred continuously. When precipitation is complete, continue the boiling for a few minutes and stir the solution without interruption as long as it is boiling. Then stand it in a warm place until the precipitate has thoroughly settled and the supernatant liquid is clear. Decant the clear liquid through a filter, add about 100 cubic centimeters of hot water and a few drops of dilute sulphuric acid, heat to boiling, allow the precipitate to settle, and again decant the clear liquid through the filter. Repeat this washing with hot water and a few drops of sulphuric acid, and then wash once by decantation with hot water alone. Then wash the precipitate on to the filter, and continue the washing on the filter with hot water until a small test of washings does not assume a milky appearance when treated with barium chloride. Dry the precipitate thoroughly, remove it to a watch glass, and burn the filter in a weighed porcelain crucible. To the ash in the crucible add a drop of fuming nitric acid or of concentrate sulphuric acid, and heat cautiously to drive off the excess of acid. When the crucible has become cool, add the main precipitate and ignite for 10 minutes at a rather low red heat over a Bunsen burner. Cool in a desiccator and weigh as barium sulphate $BaSO_4$, which contains 58.81 per cent. of barium.

43. Notes and Precautions.—Barium sulphate is a heavy, fine, white powder, which is almost absolutely insoluble in pure water (more than 400,000 parts of pure water are required to dissolve 1 part of the salt). The precipitate is much more soluble in dilute acids; hence, the solution should not contain a large amount of free hydrochloric acid,

and a large excess of the precipitant should be avoided. The precipitate has a tendency to creep up the sides of the beaker unless free hydrochloric acid is present, and if precipitated from a cold solution that does not contain free hydrochloric acid or ammonium chloride, more or less of the precipitate is almost certain to pass through the filter. The precipitate collects and settles more rapidly from hot solutions containing these compounds, and in consequence is always precipitated from such solutions. Magnesium chloride, nitrates, and especially citrates, of the alkalies, and some other compounds tend to prevent the complete precipitation of barium as sulphate; hence, solutions from which barium is to be precipitated as sulphate should be as free as possible from such compounds. The greatest objection to the determination of barium as sulphate is the tendency of the precipitate to carry other substances with it. Salts of the alkalies and alkaline earths and basic compounds of iron, aluminum, and chromium, if present in the solution, are carried down with the precipitate and can only be removed from it by patient, careful treatment. The method of washing the precipitate described in Art. **42** will generally remove nearly all these impurities, but the last traces can only be removed with the greatest difficulty. Various methods of freeing the precipitate from basic salts of iron have been proposed. Probably as good a way as any to accomplish this is to add concentrate hydrochloric acid to the precipitate, after decanting the supernatant liquid, boil off most of the excess of acid, dilute with a large quantity of water, allow the precipitate to settle, and filter. This treatment, however, will seldom be necessary if the barium is precipitated from a solution containing free hydrochloric acid and the precipitate is washed as directed in the preceding article.

Barium sulphate is partially reduced to sulphide when strongly ignited, or when ignited at a lower temperature in the presence of a reducing agent; hence, the precipitate should only be ignited at a moderate temperature over the Bunsen burner. For this reason also, the filter ash should

always be moistened with a drop of fuming nitric acid or concentrate sulphuric acid, to change back to sulphate the particles of precipitate that always adhere to the filter and are reduced to sulphide.

44. Determination of Barium as Carbonate.—Dissolve about 1 gram of pure barium chloride in about 100 cubic centimeters of water and 1 cubic centimeter of concentrate hydrochloric acid. Render the solution strongly alkaline with ammonia, heat it nearly to boiling, and precipitate the barium as carbonate with a slight excess of ammonium carbonate, adding the reagent slowly while the solution is being constantly stirred. Stand the beaker and contents in a warm place 5 or 6 hours for the precipitate to collect and settle. Decant the clear liquid through a filter, and wash once by decantation with water containing a little ammonia and ammonium carbonate. Then wash on the filter with water containing a little ammonia until a test of the washings, after being acidulated with nitric acid, does not give a precipitate with silver nitrate. Dry the precipitate, remove it to a watch glass, and cautiously burn the filter in a weighed porcelain crucible. Add the precipitate as soon as the crucible is cool and ignite at a low red heat for 10 minutes over the Bunsen burner. Cool the crucible and precipitate in a desiccator and weigh as barium carbonate $BaCO_3$, which contains 69.56 per cent. of barium.

45. Notes and Precautions.—When ammonium carbonate is added to a barium solution, barium carbonate separates as a white amorphous precipitate, which very soon changes to a crystalline powder. The precipitate is slightly soluble in pure water, and dissolves much more readily in water containing carbonic acid or ammonium chloride. This solubility, however, is largely overcome by adding ammonia to the solution. The precipitate is less soluble in hot than in cold water, and is almost absolutely insoluble in water containing ammonia and ammonium carbonate. The precipitation of barium as carbonate is hindered by the presence of citrates or metaphosphates of the alkalies.

Barium carbonate, when precipitated from solutions containing magnesium, is liable to carry down some magnesium carbonate with it, and salts of the alkalies are also carried down to a certain extent; hence, when precipitated from solutions containing these metals, the precipitate should be thoroughly washed. It remains unaltered in the air, even when heated to low redness, but at a higher temperature it begins to give off carbon dioxide and gradually changes to barium oxide. It is very difficult to change the precipitate completely to oxide, hence it is seldom, if ever, weighed as such. The results obtained by this method are usually a trifle low, but are sufficiently accurate for ordinary purposes.

ALUMINUM.

46. Determination of Aluminum as Oxide.—Dissolve from 1 to 1.5 grams of potassium alum $AlK2SO_4, 12H_2O$ in from 100 to 150 cubic centimeters of water, depending on the weight of sample taken. Add 1 cubic centimeter of concentrate hydrochloric acid and 10 cubic centimeters of ammonium chloride, heat to boiling, and precipitate the aluminum with dilute ammonia, added in very slight excess while stirring the solution continuously. When the precipitation is complete, remove the solution immediately from the flame and stand it in a warm place for the precipitate to settle, taking care that the liquid remains ammoniacal, but avoiding a large excess of ammonia. Wash the precipitate once or twice by decantation with hot water (decanting the clear liquid through a filter), and then wash on the filter with hot water until a test of the washings acidified with nitric acid fails to give a precipitate with silver nitrate. Dry the precipitate, remove it as completely as possible to a watch glass, and burn the filter in a porcelain or platinum crucible. Add the precipitate, heat gently over the Bunsen burner at first, but gradually raise the temperature, and finally ignite for 10 minutes at the full power of the blast lamp. Cool in a desiccator, and weigh as aluminum oxide Al_2O_3, which contains 53.40 per cent. of aluminum.

47. Notes and Precautions.—Aluminum hydrate, when recently precipitated, is a gelatinous translucent compound, which is rather difficult to filter at best and causes much trouble if not properly treated. The precipitate should be allowed to entirely settle, and the supernatant liquid should be poured through the filter as completely as possible before any of the precipitate is brought on to the filter, for the precipitate tends to clog the filter and make filtration very slow.

Many organic compounds interfere with the complete precipitation of aluminum as hydrate; hence, the solution from which it is to be precipitated should be as free from organic matter as possible. Hydrates of the fixed alkalies dissolve aluminum hydrate quite freely, and an excess of ammonia dissolves it sparingly, but its solubility in these is much lessened by the presence of ammonium chloride; hence, a solution from which aluminum is precipitated should always contain considerable ammonium chloride. The precipitate, when recently formed, is also dissolved freely by dilute hydrochloric acid; but it is almost entirely insoluble in pure water or water made faintly alkaline with ammonia and containing ammonium chloride. Some chemists prefer to precipitate the aluminum with considerable excess of ammonia, and then boil the solution to expel the excess of the reagent, when the aluminum hydrate at first dissolved by the ammonia will again separate. This may be done if the precipitation is made in a porcelain dish, but aluminum is generally precipitated in a beaker, and the ammonium salts present in the solution always attack the glass during the boiling and dissolve appreciable quantities of the glass, which will be weighed with the precipitate. Whichever method is employed, care must be taken to keep the solution faintly ammoniacal. If much ammonia is present, it will dissolve some of the precipitate, and if the ammonia is all driven off, the solution becomes acid, and part of the precipitate is dissolved by the acid.

Aluminum hydrate always carries down some ammonium chloride with it, and if this is not washed out, aluminum

chloride will be formed and volatilized when the precipitate is ignited. When the precipitate is ignited, water is driven off and aluminum oxide Al_2O_3 is formed. The ignition must be gentle at first or the precipitate will decrepitate, and some of it will probably be lost, but it must finally be ignited at the highest power of the blast lamp in order to drive off all the water and sulphuric acid which generally remains in the precipitate. The precipitate, if pure, remains unaltered even at a white heat, and is not reduced when ignited in the presence of hydrogen or carbon. For this reason, the filter is often wrapped around the precipitate, both placed in a crucible, and the paper burned off over a Bunsen burner, the precipitate being then ignited over the blast lamp. The only objections to this method are the difficulty sometimes experienced in getting the filter completely burned, and the increased danger of loss until the operator has gained some experience in chemical manipulation.

CHROMIUM.

48. Determination of Chromium as Oxide.—Dissolve about .5 gram of thoroughly dried potassium bichromate $K_2Cr_2O_7$ in 100 cubic centimeters of water in a porcelain dish, add 10 drops of concentrate hydrochloric acid and 5 cubic centimeters of alcohol, and heat the solution to boiling. Keep the solution at the boiling temperature, and stir it well until it is completely reduced to chromium chloride $CrCl_3$, replenishing the alcohol once or twice, and also the acid, if necessary. Complete reduction is indicated by a deep-green color, free from any yellowish tinge. After reduction is complete, continue the boiling until the excess of alcohol and the aldehyde formed by the oxidation of alcohol have been expelled, which is indicated when the odor of alcohol or aldehyde can no longer be noticed above the boiling solution. Now dilute the solution to a volume of about 150 cubic centimeters, heat it to boiling, and precipitate the chromium as hydrate, with dilute ammonia added slowly and in slight excess while

the solution is stirred continuously. Continue the boiling for a few moments, while stirring the solution, and then remove the heat and let the precipitate settle. If the supernatant liquid has a reddish tinge, the boiling must be continued until the precipitate will settle, leaving a perfectly colorless solution. Wash the precipitate once by decantation with hot water, and then wash thoroughly on the filter with hot water. Dry the precipitate, remove it to watch glass, and burn the filter in a porcelain or platinum crucible. When the crucible becomes cool, add the precipitate and ignite, gently at first, but gradually raise the temperature, and finally heat for 10 minutes at the highest temperature of the Bunsen burner. Cool the crucible and precipitate in a desiccator, and weigh as chromium oxide Cr_2O_3, which contains 68.62 per cent. of chromium.

49. Notes and Precautions.—The method given for the reduction of the chromate is probably the one most frequently used, but many chemists prefer to substitute sulphurous acid for alcohol. This method has some advantages, and the student should make one determination reducing the chromium in this way. In fact, whenever two methods of procedure are suggested, it is best to try both, and keep a record showing which method is most satisfactory. Such a record will be useful in subsequent work.

Chromium hydrate resembles aluminum hydrate in its properties. It is not so difficult to filter as aluminum hydrate, but if not carefully handled will cause much trouble. As much of the liquid as possible should be poured through the filter before any of the precipitate is allowed to come on it, or the filtration will be very slow. The separation of the precipitate is promoted by the presence of ammonium chloride, but it is best to avoid large quantities of ammonium chloride in the solution from which chromium is precipitated, as it is very difficult to wash it all out of the precipitate. Compounds of the fixed alkalies cling to the precipitate so tenaciously that, when chromium is precipitated from solutions containing large quantities of alkali salts, it is necessary,

after filtering, to dissolve the precipitate in hydrochloric acid and reprecipitate it from this solution by means of ammonia in order to get the precipitate free from salts of the alkalies.

Chromium hydrate is almost absolutely insoluble in pure water or water that is very faintly alkaline with ammonia, but if any considerable amount of free ammonia is present, the precipitate is dissolved to quite an appreciable extent, giving the solution a reddish tinge. The chromium hydrate thus held in solution may be precipitated by boiling off the excess of ammonia, but the boiling must not be continued too long, or the solution may become acid, and the precipitate will be dissolved in the acid solution. When the precipitate is ignited, water is driven off and it is changed to chromium oxide. The ignition should be gentle at first, and the temperature should be raised gradually, to prevent the loss of precipitate while water is being expelled. When the precipitate is ignited at a moderate temperature, dark-green chromium oxide is formed. If more strongly ignited, the precipitate becomes incandescent and the color changes to lighter green, but the weight remains unchanged. The precipitate is not reduced, if carefully ignited in the presence of carbon; hence, the precipitate and filter may be placed in the crucible together and carefully ignited.

ZINC.

50. Determination of Zinc as Oxide.—Dissolve a little more than 1 gram of the double sulphate of zinc and potassium $ZnK_2 2SO_4, 6H_2O$ in about 150 cubic centimeters of water, in a porcelain dish. Heat the solution to boiling, and precipitate the zinc as basic carbonate by adding sodium carbonate, drop by drop, with continuous stirring, until the solution shows a strong alkaline reaction. Continue the boiling for 5 or 10 minutes, and then let the precipitate completely subside. Decant the clear liquid through a filter, add hot water to the precipitate, and heat this to boiling. Repeat the washing by decantation once or twice, and then

wash on the filter with hot water. Dry the precipitate, remove it as completely as possible to a watch glass, and burn the filter in a porcelain crucible, taking care to heat the crucible only as high as is necessary to burn the filter. When the crucible cools, add the precipitate and ignite with a gradually increasing temperature, finally heating for 10 minutes at the highest temperature obtainable with a Bunsen burner. Cool in a desiccator and weigh as zinc oxide ZnO, which contains 80.26 per cent. of zinc.

51. Notes and Precautions.—Basic zinc carbonate is almost insoluble in pure water or water containing small quantities of sodium carbonate. It is dissolved by acids, alkaline hydrates, or bicarbonates, and ammonium compounds, but is almost completely reprecipitated from dilute solutions containing alkaline hydrates by boiling. Boiling with a moderate excess of the reagent also reprecipitates most of it from solutions containing rather small quantities of ammonium salts. Solutions from which zinc is to be precipitated as carbonate should not contain much free acid, as this sets carbon dioxide free, forming bicarbonates, which hinder the formation of the precipitate. Whenever carbon dioxide is set free, the boiling should be continued until it is completely expelled from the solution.

The precipitate carries down some of the reagent with it, but this may be removed by thorough washing with hot water, and this is much more easily accomplished by washing two or three times by decantation and then washing on the filter, than by washing entirely on the filter. At a red heat, the basic zinc carbonate is converted into zinc oxide, which is not volatile when heated alone, but is easily reduced to metallic zinc, which is volatile if heated in the presence of reducing agents. If carefully performed, this method yields quite accurate results; but they are usually a trifle low, as the precipitation of zinc as basic carbonate is never absolutely complete, and as particles of the precipitate always adhere to the filter, which exposes them to the chance of reduction and volatilization during ignition.

52. Determination of Zinc as Pyrophosphate.—Dissolve a little less than 2 grams of zinc-potassium sulphate $ZnK_2 2SO_4, 6H_2O$ in about 150 cubic centimeters of water, and add a few drops of sulphuric acid and 25 or 30 cubic centimeters of a cold saturated solution of microcosmic salt $HNaNH_4PO_4$. Heat the solution to boiling, and precipitate the zinc as zinc-ammonium phosphate $ZnNH_4PO_4$ by adding ammonia slowly to slight excess, while the solution is stirred continuously. Continue the boiling, while stirring vigorously and without interruption, until the solution is as near as possible to the point of exact neutrality. If the solution bumps when heated over the flame, it must be removed to a water bath and heated, with frequent stirring, until the excess of ammonia is expelled and the precipitate becomes crystalline. Allow the precipitate to settle completely, wash once by decantation with hot water, and then wash on the filter with hot water until a test of the washings is free from phosphoric acid. Dry the precipitate, remove it as completely as possible from the filter to a watch glass, and burn the filter in a porcelain crucible, avoiding excessive heat. When the crucible becomes cool, add the precipitate and ignite, gently at first, but gradually increase the temperature, and finally heat intensely for 10 minutes. Cool in a desiccator, and weigh as zinc pyrophosphate $Zn_2P_2O_7$, which contains 42.77 per cent. of zinc.

53. Notes and Precautions.—Zinc-ammonium phosphate when first precipitated is a white flocculent solid, but it soon becomes crystalline when boiled and stirred. It is soluble in acids and in ammonia or ammonium compounds, but its solubility in the latter is greatly diminished by the use of a large excess of the microcosmic salt. About three times the amount of this reagent that will be required to unite with the zinc should be added to the solution. Ammonia should only be added in slight excess, and it is best to boil off most of this excess over the burner, if possible, but the solution containing this precipitate frequently bumps so vigorously, even when stirred constantly, that it is

necessary to drive off the excess of ammonia over the water bath. It is better that the solution should remain faintly alkaline than that it should be acid, for in the presence of a large excess of the precipitant, the zinc separates almost completely from a faintly alkaline solution. A large excess of ammonium chloride or acetate should be particularly avoided. The precipitate is washed quite easily. It is thoroughly cleaned when a test of the washings no longer gives a precipitate with ammonium molybdate or with magnesium sulphate to which ammonium chloride is added. When the zinc-ammonium phosphate is ignited, it gives off ammonia NH_3 and water and is converted into zinc pyrophosphate. The heat should be applied gradually, or some of the precipitate may be lost during this change. The precipitate should be removed as completely as possible from the filter paper before ignition, for particles adhering to the paper are liable to be reduced and volatilized during ignition. This method yields very accurate results when carefully handled, and is probably the most satisfactory method in all cases that admit of its use.

54. Determination of Zinc as Sulphide.—There are several methods of determining zinc as sulphide. Two of the methods in most general use are here given:

1. Dissolve about 1.5 grams of zinc-potassium sulphate in 150 cubic centimeters of water in a flask having a capacity of about 250 cubic centimeters. Add 20 cubic centimeters of ammonium chloride, and then add ammonium hydrate, drop by drop, until the solution is slightly alkaline. Warm the solution gently, add ammonium sulphide in sufficient quantity to precipitate the zinc, give the flask a rotary motion to mix the contents, fill to the neck with water, stopper tightly, and stand it in a warm place for at least 12 hours for the precipitate to collect and settle. Decant the clear liquid through a filter, and wash the precipitate by decantation with hot water containing a little ammonium sulphide and ammonium chloride. Then bring the precipitate on to the filter and wash at first with hot water containing ammonium sulphide

and ammonium chloride, and then with water containing only a small quantity of ammonium sulphide. Dry the precipitate, remove it to a watch-glass, and burn the filter in a Rose crucible. Add the precipitate, sprinkle a little powdered sulphur over it, and ignite in a stream of hydrogen, as directed in Art. **18**, except that in this case the precipitate should not be ignited over the blast lamp. Ten minutes' ignition at the highest temperature of the Bunsen burner is sufficient. Cool the precipitate in a stream of hydrogen and weigh as zinc sulphide ZnS, which contains 67.03 per cent. of zinc.

2. Dissolve about 1.5 grams of zinc-potassium sulphate in 150 or 200 cubic centimeters of water, add 20 to 25 cubic centimeters of ammonium chloride, and then add ammonia, drop by drop, until the solution is slightly alkaline. If a precipitate separates at this point, dissolve it in the least necessary amount of acetic acid. Heat the solution to boiling, and precipitate the zinc as sulphide by leading a rapid current of hydrogen sulphide through the gently boiling solution for half an hour. Allow the precipitate to settle, wash twice by decantation with hot water containing hydrogen sulphide and a little ammonium chloride, and then wash on the filter with hot water containing hydrogen sulphide. The precipitate should not be washed excessively on the filter. Dry, and ignite in a current of hydrogen as in the first method.

55. Notes and Precautions.—Zinc may be precipitated as sulphide from neutral or alkaline solutions, or those that are acid with an organic acid—especially acetic acid. It is practically insoluble in water, alkalies, or organic acids, but the formation of the precipitate is retarded by free organic acids and by ammonia; hence, the solution is usually made as near neutral as possible before precipitating. Ammonium chloride aids the separation of the precipitate in a granular form, in which condition it is most readily washed. The precipitate is dissolved, or its formation is prevented, by mineral acids. Hydrochloric acid has the greatest solvent effect, and sulphuric acid has the least.

The precipitate has a great tendency to run through the

filter, especially if the solution contains free ammonia; to avoid this, the solution is sometimes rendered alkaline with sodium carbonate, and then just acidified with acetic acid before precipitation. Ammonium chloride is frequently added to the first portion of wash water to keep the precipitate in a granular condition. After all impurities are washed out, the precipitate tends to change from the granular to a slimy form, in which condition it will pass through the filter, if the washing is continued; hence, excessive washing is to be avoided. Heat aids the separation of the precipitate, but increases the action of solvents on it.

Zinc may be precipitated from acetic-acid solutions by ammonium sulphide, as well as by hydrogen sulphide; hence, if a precipitate is formed when the solution from which zinc is to be precipitated by ammonium sulphide is rendered alkaline, it may be dissolved in the least necessary quantity of acetic acid, and the zinc be precipitated from this acidulated solution. Zinc sulphide is slowly oxidized to soluble zinc sulphate by the action of the air; hence, the precipitate should be protected from the air as much as possible during washing, etc. But, if the determination is carried through with as little delay as possible, there is slight danger of loss from this source. The precipitate must be removed from the filter as completely as possible, or some of the zinc will be reduced to the metallic state and volatilized while burning the paper. The ignition in hydrogen should be performed as directed in Art. **18**, except that it is best not to use the blast lamp. Ten minutes' ignition at the full power of the Bunsen burner is sufficient. If the blast lamp is used, the highest power should not be employed, and the ignition should only be continued about 5 minutes. The precautions to avoid an explosion, mentioned in Art. **19**, should be observed.

ARSENIC.

56. Determination of Arsenic as Sulphide.—Weigh about .5 gram of arsenious oxide As_2O_3 into a flask of 250 or 300 cubic centimeters capacity, and dissolve it in 25 cubic

ntimeters of concentrate hydrochloric acid, with the aid of ntle heat, but taking care not to heat near the boiling int. More hydrochloric acid may be used, if the quantity first added is insufficient. When solution is complete, ute with water to half the capacity of the flask, and fit it th a doubly perforated stopper, as shown in Fig. 9. Through e perforation, pass a tube *a* reach- g nearly to the bottom of the flask d drawn out to a small opening at e lower end. Through the other rforation, pass a tube *b* reaching st through the stopper. Bend both these tubes at right angles above e stopper. Through the tube *a* con- ct a gentle current of hydrogen sul- ide, which has been washed by ssing through water for an hour. low the flask to stand stoppered for hour, and then remove the excess hydrogen sulphide by leading car- n dioxide through the liquid in the ne way that the hydrogen sulphide was passed through. om half an hour to an hour suffices to accomplish this. low the precipitate to settle, and filter through a weighed er as described in Art. **27.** Wash rapidly and thoroughly the filter with warm (not hot) water, occasionally adding a v drops of hydrogen-sulphide solution. Dry at 100° to 105° til a constant weight is obtained. The precipitate should w be arsenious sulphide As_2S_3, which contains 60.98 per nt. of arsenic.

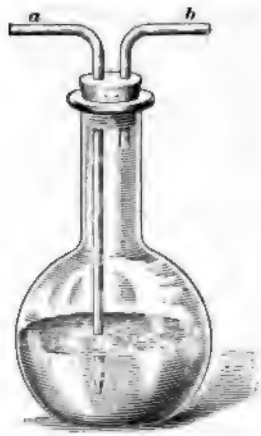

FIG. 9.

57. Notes and Precautions.—Arsenic is precipitated sulphide from a solution that is strongly acid with hydro- loric acid. If the arsenic is all in the arsenious condition, d no reducible compounds are present, the precipitate ould be pure; but if reducible compounds are present—as, instance, arsenic or ferric salts—free sulphur will be rown out during their reduction, and will remain mixed

with the precipitate. If the precipitate is formed in the cold, this will remain in a finely divided state and may be washed out. The precipitate separates from a warm solution more readily than from a cold one, and if the solution is such that there is no danger of separation of sulphur, the solution may be heated to about 60° during precipitation, but should not be heated above 70°, for fear of volatilizing some of the arsenic. If, however, the solution is such that sulphur is liable to be thrown out, precipitation should be made in the cold, for heat causes the sulphur to assume a form that is very difficult to remove from the precipitate. It is best to remove the excess of hydrogen sulphide from the flask by means of carbon dioxide, as directed, but this may be done by connecting the tube *b* with an aspirator and drawing air through the solution. The only objection to this method is that air tends to decompose hydrogen sulphide, and a little sulphur may thus be set free.

It sometimes happens that particles of the precipitate adhere to the glass so tenaciously that they cannot be removed from the flask by mechanical means. In such cases, dissolve the portion of the precipitate adhering to the glass in a little ammonia, reprecipitate by rendering the solution distinctly acid with hydrochloric acid, and add this to the main precipitate on the filter. Care must be taken that only acid or neutral solutions come in contact with the precipitate, for it is soluble in alkaline hydrates, sulphides, and carbonates, and also in strong nitric acid or aqua regia, but is practically insoluble in hydrochloric and sulphuric acids.

If there is reason to suspect that the precipitate may contain free sulphur, it should be washed with carbon bisulphide, which will dissolve the free sulphur. If the precipitation was made in the cold, this may be accomplished by washing thoroughly on the filter with carbon bisulphide, after washing once or twice with strong alcohol, and then again washing two or three times with strong alcohol. Many chemists prefer to always wash the precipitate in this way, in order to avoid the possibility of free sulphur being present. If the arsenic is precipitated from a hot solution

and sulphur separates, it cannot be removed by washing on the filter. In this case, the precipitate must be removed to a porcelain dish and digested with carbon bisulphide on a water bath for some time, replenishing the carbon bisulphide from time to time and taking care not to allow the mixture to evaporate to dryness. The precipitate may now be transferred to a weighed filter and washed twice on the filter with carbon bisulphide, and then two or three times with strong alcohol.

The precipitate must be dried until a constant weight is obtained. This may take some time, as the last portions of water are driven off slowly, and the temperature must not be allowed to rise very much, for the precipitate is easily volatilized without change of composition.

58. Determination of Arsenic as Magnesium Pyroarsenate.—Dissolve about .5 gram of arsenious oxide in the least necessary quantity of concentrate hydrochloric acid in a beaker by the aid of gentle heat, but taking care not to allow the temperature to rise above 70°. When all is dissolved, add potassium chlorate, a few crystals at a time, until the solution emits a strong odor of chlorous acid, and then allow it to stand on the water bath at about this temperature until the odor of chlorous acid has almost entirely disappeared. Complete oxidation to arsenic acid is thus effected. Dilute the solution to about 100 cubic centimeters, render it distinctly alkaline with ammonia, and precipitate the arsenic, as magnesium-ammonium arsenate, with a moderate excess of magnesia mixture,* adding the reagent slowly and with constant stirring. Now add from 15 to 20 cubic centimeters of concentrate ammonia, stir well, cover the beaker, and allow it to stand in a cold place for 12 hours. Filter, and wash on the filter with a cold solution, containing 1 part of concentrate ammonia and 4 parts of water, until a test of the washings, when acidified with nitric acid, fails to

*Magnesia mixture is made by dissolving 51 grams of crystallized magnesium chloride and 100 grams of ammonium chloride in a little water, adding 208 cubic centimeters of ammonium hydrate of .96 Sp. Gr., and diluting to 500 cubic centimeters with water.

give a precipitate with silver nitrate, showing that the chlorides have been washed out of the precipitate; but avoid excessive washing. Dry the precipitate, remove it as completely as possible from the paper, place the filter in a Rose crucible, and saturate it with a concentrate solution of ammonium nitrate. Apply a gentle heat to the crucible to dry the paper, and finally raise the temperature sufficiently to burn the paper completely. When the crucible has cooled, add the precipitate, cover the crucible and lead in a rather slow stream of oxygen in the same way that hydrogen was introduced in the determination of copper as sulphide (see Art. **18**). Heat very gently at first, and raise the temperature very gradually, finally igniting for 15 minutes at the highest temperature of the Bunsen burner, or for 10 minutes over the blast lamp. Cool in a desiccator, and weigh as magnesium pyroarsenate $Mg_2As_2O_7$, which contains 48.41 per cent. of arsenic.

59. Notes and Precautions.—The same care to avoid excessive heat during solution and oxidation that was necessary in dissolving the arsenic to be precipitated as sulphide is necessary in this case, for arsenic is readily volatilized when boiled with hydrochloric acid. Magnesium-ammonium arsenate $MgNH_4AsO_4$ is a white crystalline precipitate, closely resembling magnesium-ammonium phosphate. It is slightly soluble in water and more so in ammonium chloride, especially if the solution is heated, but this solubility is largely overcome by keeping the solution cold and having present a moderate excess of the precipitant and a large excess of ammonia. As the precipitate is not entirely insoluble in dilute ammonia, it should only be washed as much as is necessary to remove the impurities.

When ignited in the presence of carbon, the precipitate is reduced; hence, the filter should always be saturated with a strong solution of ammonium nitrate to supply oxygen and thus prevent reduction and consequent volatilization of the particles of precipitate adhering to the paper. If this precipitate is ignited in the ordinary manner, the ammonia and

water, while passing off, will usually carry some of the precipitate with them; and the ammonia, during its rapid evolution, partially reduces the arsenic, which is then volatilized by the heat. These sources of error are eliminated by igniting the precipitate in oxygen and raising the temperature very gradually, as directed. If a convenient source of oxygen is not at hand, the same end may be attained by the following method: After transferring the precipitate to a crucible, place this in an air bath and heat it for an hour at about 130°. Then transfer the crucible to a thin iron plate placed over the burner, keeping it at first at the same temperature as the air bath, and then gradually increasing the heat until, at the end of 2 or 3 hours, the plate shows a faint redness. The crucible containing the precipitate may now be removed to a tripod and ignited over a burner at a gradually increasing temperature, finally heating for 15 minutes at the highest power of the Bunsen burner, or 10 minutes over the blast lamp. The crucible should always be covered during ignition, to prevent loss. After the precipitate has been converted into pyroarsenate, it may be heated at the full power of the blast lamp without decomposition, but this high temperature is not necessary. The highest power of the Bunsen burner is sufficient.

ANTIMONY.

60. Determination of Antimony as Sulphide.—Weigh 1 gram of potassium antimony tartrate $2KSbOC_4H_4O_6, H_2O$, known as *tartar emetic*, into a flask, fitted as shown in Fig. 9. Add 1 gram of solid tartaric acid, then a little water, and finally a few drops of hydrochloric acid. Heat gently, if necessary to bring the salt into solution, but do not bring to boiling. When dissolved to a clear solution, dilute to about 150 cubic centimeters, heat to boiling, and precipitate the antimony as sulphide by leading a current of washed hydrogen sulphide through the gently boiling solution in the same way that it was conducted through the arsenic solution (see Art. **56**). The antimony will generally be completely

precipitated in half an hour. Allow it to stand for half an hour in a warm place, and then pass a current of carbon dioxide or air through the solution for half an hour to remove the excess of hydrogen sulphide, as was done in the determination of arsenic as sulphide. After the precipitate has settled, wash two or three times by decantation with hot water containing a little hydrogen sulphide, decanting the clear liquid through a filter that has been dried and weighed. Then bring the precipitate on to the filter and continue to wash with hot water containing hydrogen sulphide, adding a fresh supply of wash water as soon as the previous portion has run through the filter, in order to protect the precipitate from the air as much as possible. Dry the precipitate in the air bath at 100° to 105° until a constant weight is obtained. The precipitate is now composed of a variable mixture of antimony sulphide, sulphur, and water, and a correction must be made. There are two methods of doing this, and the student should do one each way.

1. Weigh a porcelain boat, place in it a convenient quantity of the precipitate, taking care not to get any particles of filter paper mixed with it, and weigh it again, thus ascertaining the weight of the precipitate taken for treatment. Place this in a hard-glass tube, as shown in Fig. 6, *Qualitative Analysis*, Part 2, and lead in dry carbon dioxide. When the tube is completely filled with carbon dioxide, bring a Bunsen burner under the boat and heat, gently at first, but gradually raise the temperature, while continuing the current of carbon dioxide, until all water and sulphur are driven off. Allow the precipitate and boat to cool in the current of carbon dioxide; then remove from the tube and weigh again. The precipitate is now Sb_2S_3, and from this weight the weight of Sb_2S_3 in the original precipitate may be calculated by a simple proportion. If we represent the weight of the original precipitate by a, the weight of the portion taken for correction before heating by b, and the weight of the portion taken for correction after heating by c, we have $b : c = a : x$. $x = Sb_2S_3$ in the original precipitate, and contains 71.76 per cent. of antimony.

2. Weigh a convenient amount of the precipitate into a Rose crucible, and by means of a dropper add 2 drops of concentrate nitric acid through the perforation in the cover. Then, using the dropper, add fuming nitric acid, drop by drop, in sufficient quantity to cover the precipitate, taking care not to add the acid rapidly enough to excite too violent action. Warm the crucible very gently over the water bath until all sulphur and sulphide have been oxidized, replenishing the fuming acid if necessary and taking care not to heat sufficiently to fuse the sulphur. When all is oxidized, evaporate the excess of acid over the water bath, and then heat over the Bunsen burner, very gently at first, and gradually raise the temperature until the crucible just shows a faint redness. Cool in a desiccator and weigh. Then heat again at about the same temperature, and continue this treatment until a constant weight is obtained. The precipitate is now Sb_2O_4, and from this the weight of antimony in the original precipitate may be readily calculated. The percentage of antimony in Sb_2O_4 is given as 79.22.

61. Notes and Precautions.—Antimony and its compounds are rather difficult to dissolve, and no exact directions for dissolving can be given, for treatment that succeeds in one case may fail in another. With a little care and patience, however, antimony may usually be obtained in solution without a great deal of trouble. Tartaric acid helps to dissolve the salt, prevents the separation of white antimony oxychloride $SbOCl$ when the solution is diluted, and promotes precipitation as sulphide; hence, it is always added to the sample. Antimony is most readily precipitated from a boiling solution; hence, if the solution is one that will permit, it is boiled gently during precipitation. If the solution contains nitric acid or a large quantity of hydrochloric acid, the solution cannot be boiled, as there is danger of volatilizing the antimony, and the solvent action of these acids is greatly increased by heat. The precipitate is dissolved to a greater or less extent by alkalies and alkaline sulphides; hence, it should always be precipitated from acid solutions. A large excess of acid should be avoided,

as the precipitate is not altogether insoluble in strongly acid solutions, especially when they are heated. The precipitate is not readily acted on by the air, but should not be unnecessarily exposed during washing, or some loss may occur.

In making the correction by the first method, the temperature should be carefully regulated. The precipitate must be heated strongly enough to drive off the water and sulphur, but if heated too strongly, the sulphide of antimony will also be volatilized. In working by the second method, the acid should be added very slowly and carefully to avoid loss by spattering, and also to avoid excessive heat. Care must also be taken to avoid too high a temperature when heating over the water bath, until the sulphur is completely oxidized, or it will fuse and form globules, which are almost impossible to oxidize. Common concentrate nitric acid will not oxidize the sulphur, but nearly always causes it to fuse into globules. Red fuming nitric acid accomplishes the oxidation quite readily, but it is best to moisten the precipitate with a drop or two of the common concentrate acid before adding the fuming acid, in order to prevent too violent action at first.

POTASSIUM.

62. Determination of Potassium as Potassium-Platinum Chloride.—Dissolve about .5 gram of potassium chloride KCl in 2 or 3 cubic centimeters of water, in a small porcelain dish, and precipitate the potassium with a slight excess of platinum-chloride solution. Place the dish on a water bath, and evaporate nearly to dryness, without allowing the water in the bath to quite reach the boiling point, thus avoiding too strong a heat. When almost dry, add 30 or 40 cubic centimeters of alcohol, having a strength of about 80 per cent. by volume, and let stand for an hour, stirring occasionally. Then proceed according to one of the following methods:

1. Decant the alcohol through a weighed filter and wash twice by decantation with alcohol of the same strength.

Then bring the precipitate on to the filter and continue the washing with alcohol until the impurities are completely removed, but avoid excessive washing. Dry the filter and precipitate at 130° until a constant weight is obtained. The precipitate is potassium-platinum chloride K_2PtCl_6.

2. Decant the clear liquid through a filter, wash twice by decantation with alcohol, and then wash on the filter with alcohol of the same strength. Dry the precipitate, remove it as completely as possible from the filter to a watch glass, taking care not to get any particles of paper mixed with it, replace the filter in the funnel, and dissolve any precipitate adhering to it by washing it with hot water, receiving this solution in a small, weighed dish, preferably of platinum. Evaporate this to dryness over a water bath, add the main precipitant, and heat at 130° in an air bath, until a constant weight is obtained. The precipitate is K_2PtCl_6, which contains 16.03 per cent. of potassium.

63. Notes and Precautions. — Potassium-platinum chloride is a reddish-yellow crystalline compound, which dissolves readily in water, alkalies, or acids, but is only slightly soluble in an 80-per-cent. solution of alcohol, and is almost entirely insoluble in absolute alcohol. On account of the solubility of the precipitate in water, only a very small amount of water should be used in dissolving the sample, and most of this should be evaporated off after adding the precipitant, and before adding the alcohol. In driving off the water, only a gentle heat should be used, in order to avoid the danger of decomposing the reagent and weighing some metallic platinum as potassium-platinum chloride.

The precipitate should be thoroughly washed, but the washing should not be continued after the impurities are removed, as the precipitate is not entirely insoluble in 80-per-cent. alcohol, and absolute alcohol cannot be used for washing, as the precipitate may contain impurities that are insoluble in absolute alcohol. This is especially true if the potassium was precipitated from a solution containing

sulphates or sodium compounds. A slight excess of the precipitant diminishes the solubility of the precipitate, and the same may be said of sodium compounds, but the advantage derived from having much of either of these present is counterbalanced by the increased washing they occasion. Upon heating for some time at 130° all the water is driven off, and the precipitate may be weighed as K_2PtCl_6. If strongly ignited, the precipitate is decomposed, forming principally potassium chloride and metallic platinum. For this reason, the precipitate should not be heated much above 130°.

AMMONIUM.

64. Determination of Ammonium as Ammonium-Platinum Chloride. — **Dissolve .5 gram of pure, dry ammonium chloride NH_4Cl in 2 or 3 cubic centimeters of water, and proceed exactly as in the determination of potassium (Art. 62). Weigh as ammonium-platinum chloride $(NH_4)_2PtCl_6$, which contains 8.09 per cent of ammonium NH_4.**

65. Notes and Precautions.—Ammonium-platinum chloride resembles potassium-platinum chloride very closely, both in appearance and chemical properties, but is rather lighter in color, dissolves more readily, and is more easily decomposed by heat than the potassium compound. It is rather less soluble in alcohol containing ether than in alcohol alone; hence, a solution consisting of 3 parts of 80-per-cent alcohol and 1 part of pure ether is sometimes used to wash it. It may be dried at 130° without decomposition, but the temperature should not be allowed to rise above this point.

After weighing this precipitate, it is a good plan to decompose it by heat and weigh the metallic platinum as a check on the results obtained. If the precipitate is weighed on a filter, remove it as completely as possible to a watch glass, and cautiously burn the filter in a porcelain crucible. When cold, add the precipitate and heat, gently at first, but

gradually raise the temperature until all the volatile parts are expelled and metallic platinum remains in the crucible. Cool in a desiccator and weigh. If the precipitate is removed from the filter and weighed in a dish, as directed in the second method, Art. **62,** a porcelain crucible should be used. Then, after drying at 130° and weighing, the precipitate may be ignited at a gradually increasing temperature to drive off the volatile constituents, and the platinum may be weighed as a check on the first result. In either case, the ignition should be conducted very cautiously and the temperature should be raised very gradually, for if suddenly and strongly ignited, the escaping chlorine and ammonium chloride will carry particles of the original precipitate and finely divided platinum with them, and thus give too low a result. The weight of ammonium may be calculated from the weight of the platinum by a simple proportion, as follows:

$$Pt : (NH_4)_2 = \text{wt. of } Pt : x.$$

SULPHURIC ACID.

66. Determination of Sulphuric Acid as Barium Sulphate.—Dissolve about 1 gram of pure copper sulphate $CuSO_4,5H_2O$ in 200 cubic centimeters of water, and add 1 cubic centimeter of dilute hydrochloric acid and 10 cubic centimeters of ammonium chloride. Heat the solution to boiling, and precipitate the sulphuric acid with a solution of barium chloride, adding the reagent very gradually and in but slight excess to the boiling solution, while it is stirred continuously. When precipitation is complete, remove the beaker and contents to a warm place—preferably a water bath—and allow it to stand for 2 or 3 hours, keeping the solution near the boiling point. When the precipitate has completely settled, decant the clear liquid through a filter, add hot water, bring to boiling, allow the precipitate to settle, and repeat the washing by decantation, in this manner, two or three times. Then bring the precipitate on to the filter, and wash with hot water until a test of the washings fails to

give a reaction for chlorine when acidified with nitric acid and treated with silver nitrate. Dry the precipitate, remove it as completely as possible from the filter to a watch glass, and burn the filter in a porcelain crucible. When the crucible becomes cool, add a drop or two of concentrate sulphuric acid to the ash, heat gently to drive off the excess of acid, and then gradually increase the temperature until the crucible assumes a dull-red color. Allow the crucible to cool, add the precipitate, place the cover on the crucible, and ignite at a gradually increasing temperature, finally heating at a moderate red heat for 10 minutes. Cool the crucible and precipitate in a desiccator and weigh as barium sulphate $BaSO_4$, which contains 34.33 per cent. of SO_3, or 41.20 per cent. of SO_4, and is equivalent to 42.06 per cent. of its weight of H_2SO_4.

67. Notes and Precautions.—The properties of barium sulphate have been given in Arts. **42** and **43**, which should be read in connection with this determination. The precipitate is less likely to run through the filter when precipitated from a hot solution containing a little free hydrochloric acid and some ammonium chloride, as it appears to assume a denser form under these conditions. The precipitate is also rendered more dense by allowing it to stand at a temperature near the boiling point for a few hours before filtering. The solution should contain but little free hydrochloric acid and no nitric or chloric acid, as all of these dissolve more or less of the precipitate, if present in large amount; and nitric and chloric acids form nitrates and chlorates, which are very difficult to remove from the precipitate. If these latter acids are present in the solution, it should be evaporated repeatedly on the water bath with pure hydrochloric acid, until they are completely expelled. Then dilute with water and precipitate as directed.

In the determination of sulphuric acid, the percentage of SO_3 is usually required. Sometimes, however, the percentage of SO_4, and occasionally of H_2SO_4, is required; hence, the factors for all of these are given.

PHOSPHORIC ACID.

68. Determination of Phosphoric Acid as Magnesium Pyrophosphate.—Dissolve about .6 gram of pure, dry microcosmic salt $HNaNH_4PO_4, 4H_2O$ in 100 cubic centimeters of water, add 5 or 10 cubic centimeters of ammonium chloride, and then precipitate the phosphoric acid with a slight, but sure, excess of magnesia mixture, adding the reagent very gradually, and with constant, vigorous stirring, but taking care not to allow the rod to strike the side of the beaker. When precipitation is complete, add concentrate ammonia to about one-fourth the previous volume of the liquid, stir well, and stand in a cold place 5 or 6 hours for the precipitate to collect and settle in the crystalline form. Filter, and wash on the filter with water containing one-fourth its volume of concentrate ammonia, until a test of the washings, acidified with nitric acid, does not give a reaction with silver nitrate; but avoid excessive washing. Dry the precipitate, remove it from the filter to a watch glass, and burn the filter in a porcelain crucible. After cooling, add the precipitate and again ignite at a gradually increasing temperature, finally heating for 10 minutes at full redness. Cool in a desiccator and weigh. If the precipitate is not perfectly white, add 2 or 3 drops of concentrate nitric acid, heat gently to expel the excess of acid, and then raise the temperature to full redness for 5 minutes. Cool in a desiccator and weigh as magnesium pyrophosphate $Mg_2P_2O_7$, which contains 63.97 per cent. of P_2O_5, or 42.79 per cent. of PO_4.

69. Notes and Precautions.—The precipitate in this case is the same as that obtained in the determination of magnesium, and has been described in Arts. **34** and **35**, which should be read in connection with this determination. In that case, the magnesium was precipitated by phosphoric acid, while in this case, the phosphoric acid is precipitated by magnesium. The magnesia mixture, used as the precipitant, is made as described in the foot note to Art. **58.**

VOLUMETRIC DETERMINATIONS.

GENERAL REMARKS.

70. As we have already seen, in volumetric analysis treat a substance with a solution having a known powei chemical action, and calculate the quantity of the substa present by the amount of the solution required to chang from one state to another. From this, it will be seen in making a volumetric determination we must have a st ard solution whose power of action is accurately know graduated vessel from which to introduce the solutior that the quantity taken is accurately measured, and s means of recognizing the exact point at which the reac is complete. Having these requisites, a volumetric de mination becomes a simple matter. Volumetric anal has much to commend it. As a rule, the volumetric m ods are shorter and simpler than the gravimetric; 1 appear neater in many instances, and in many cases least, the results obtained are just as accurate.

71. Standard Solutions.—The standard solution 1 in determining any element must be one whose powe action on that element is accurately known. The e strength at which the solution is used is not a matte great importance, so long as its exact strength is known, the amount of a substance changed by a given amount solution of any strength may readily be calculated from equation representing the reaction, provided the strengtl the solution is known. Of course the more dilute the st ard solution is made, within reasonable limits, the n accurately we may determine the exact amount of the ac agent in the solution that has been used to produce change; for we would have to make an error of 1 c centimeter in reading the quantity of a solution of a cer strength used, to correspond to an error of $\frac{1}{10}$ cubic ce meter when using a solution of ten times this stren

For practical reasons, however, the standard solution should not be made too dilute. When volumetric analysis first came into use, a separate solution was used for each element to be determined, and the solutions were made of such strength that when a given weight—generally 1 gram—of the sample was taken, the number of cubic centimeters of standard solution used represented the percentage of the given element in the sample. Such solutions are very handy in some ways, and are still largely used where a solution is only used to determine one element, but where the same solution is used for a number of different determinations, solutions based on a different principle are now generally used. Solutions based on atomic weights, known as normal and decinormal solutions, are now largely used, and are very handy. *A normal solution is one, a liter of which contains the atomic weight of the active element in grams.* To make such a solution, if the compound to be employed contains but 1 atom of the active element in the molecule, the molecular weight of the substance, taken in grams, is dissolved and diluted to 1 liter. Thus, a normal solution of sodium hydrate is one containing the molecular weight (40 grams) of the salt in a liter of solution, for a liter of such a solution contains the atomic weight (23) of the active element (sodium) in grams. If, however, we were to dissolve the molecular weight, in grams, of sodium carbonate Na_2CO_3 and make the solution up to 1 liter, this solution would be twice the strength of a normal one, for a liter of it would contain twice the atomic weight, in grams, of the active element, which is sodium in this case also. Hence, a normal solution of a compound, the molecule of which contains 2 atoms of the active element, contains one-half the molecular weight, in grams, of the compound in a liter.

Similarly with the acids. A normal hydrochloric-acid solution is one containing the molecular weight (36.37), in grams, of pure hydrochloric acid HCl in a liter, for this contains the atomic weight (1) of the active element (hydrogen), in grams, per liter. But, if a liter of a sulphuric-acid solution should contain the molecular weight (98) of the pure

give a reaction for chlorine when acidified with nitric acid and treated with silver nitrate. Dry the precipitate, remove it as completely as possible from the filter to a watch glass, and burn the filter in a porcelain crucible. When the crucible becomes cool, add a drop or two of concentrate sulphuric acid to the ash, heat gently to drive off the excess of acid, and then gradually increase the temperature until the crucible assumes a dull-red color. Allow the crucible to cool, add the precipitate, place the cover on the crucible, and ignite at a gradually increasing temperature, finally heating at a moderate red heat for 10 minutes. Cool the crucible and precipitate in a desiccator and weigh as barium sulphate $BaSO_4$, which contains 34.33 per cent. of SO_3, or 41.20 per cent. of SO_4, and is equivalent to 42.06 per cent. of its weight of H_2SO_4.

67. Notes and Precautions.—The properties of barium sulphate have been given in Arts. **42** and **43**, which should be read in connection with this determination. The precipitate is less likely to run through the filter when precipitated from a hot solution containing a little free hydrochloric acid and some ammonium chloride, as it appears to assume a denser form under these conditions. The precipitate is also rendered more dense by allowing it to stand at a temperature near the boiling point for a few hours before filtering. The solution should contain but little free hydrochloric acid and no nitric or chloric acid, as all of these dissolve more or less of the precipitate, if present in large amount; and nitric and chloric acids form nitrates and chlorates, which are very difficult to remove from the precipitate. If these latter acids are present in the solution, it should be evaporated repeatedly on the water bath with pure hydrochloric acid, until they are completely expelled. Then dilute with water and precipitate as directed.

In the determination of sulphuric acid, the percentage of SO_3 is usually required. Sometimes, however, the percentage of SO_4, and occasionally of H_2SO_4, is required; hence, the factors for all of these are given.

VOLUMETRIC DETERMINATIONS.

GENERAL REMARKS.

70. As we have already seen, in volumetric analysis we treat a substance with a solution having a known power of chemical action, and calculate the quantity of the substance present by the amount of the solution required to change it from one state to another. From this, it will be seen that in making a volumetric determination we must have a standard solution whose power of action is accurately known, a graduated vessel from which to introduce the solution, so that the quantity taken is accurately measured, and some means of recognizing the exact point at which the reaction is complete. Having these requisites, a volumetric determination becomes a simple matter. Volumetric analysis has much to commend it. As a rule, the volumetric methods are shorter and simpler than the gravimetric; they appear neater in many instances, and in many cases, at least, the results obtained are just as accurate.

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acid, H_2SO_4, in grams, it would contain 2 grams of hydrogen, which is the active element, and the atomic weight of hydrogen is 1. Hence, to have this solution correspond with our definition, a liter of solution must contain one-half the molecular weight, or 49 grams of pure acid. Thus, we see that to make up a normal solution of any compound, 1 liter of the solution must contain the molecular weight, in grams, of the compound, divided by the number of atoms of the active element contained in the molecule. One of the great advantages of this system of making solutions is the fact that all solutions thus made up have the same strength. Ten cubic centimeters of any normal acid solution will exactly neutralize 10 cubic centimeters of any normal alkali solution. Take, for example, hydrochloric-acid and sodium-hydrate solutions. The reaction is

$$HCl + NaOH = NaCl + H_2O$$

One molecule of one just neutralizes 1 molecule of the other, and as each solution contains the molecular weight in grams, it is evident that equal volumes of the two solutions will exactly neutralize each other. In the case of sulphuric acid and sodium hydrate, the reaction is

$$H_2SO_4 + 2NaOH = Na_2SO_4 + 2H_2O$$

One molecule of the sulphuric acid unites with 2 molecules of sodium hydrate, but as only half the molecular weight of the sulphuric acid is contained in a liter of the solution, equal volumes of these solutions just neutralize each other.

In practical work, normal solutions are usually too strong to yield very accurate results, and solutions one-tenth as strong as the normal ones are largely employed. These are called *decinormal* solutions, and are usually designated as $\frac{n}{10}$. Such solutions may be made by dissolving one-tenth as much of the compound as would be used in making a normal solution and diluting to 1 liter; or 100 cubic centimeters of a normal solution may be accurately measured out and diluted to 1 liter.

However a standard solution is made up, it must be thoroughly mixed. If a solution is diluted with water, the

original solution and the water tend to form separate layers, and one part of the solution will be much stronger than another. A perfectly uniform solution is required, and this can only be obtained by very thorough agitation. The solutions must be kept in tightly stoppered bottles, for, if left exposed to the air, some solutions will absorb moisture and become weaker, but most of them lose water by evaporation, thus becoming stronger. When thus preserved, some standard solutions will keep their strength almost indefinitely, but others always decompose slowly; hence, after a solution has stood for any considerable time, its strength should always be ascertained anew before it is used. The solutions should be kept in a cool, dark place, for heat and light—especially direct sunlight—promote decomposition.

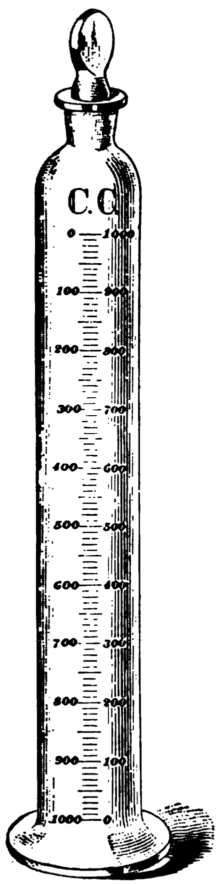

FIG. 10.

MEASURING VESSELS.

72. As in volumetric analysis all determinations depend on the quantity of solutions of known strength used, it is of the utmost importance that we have accurately graduated measuring vessels to be used in making up, and measuring out, definite quantities of these solutions. The most important of these vessels are graduated cylinders, pipettes, flasks, and burettes.

73. Graduated Cylinders.—Graduated cylinders are very largely used in making up standard solutions. For this purpose, a stoppered cylinder, graduated to 1 liter, shown in Fig. 10, is generally used, but the ordinary wide-mouth lipped cylinder is sometimes used. The form shown in Fig. 10 has an advantage in that, after the solution in the cylinder has been diluted the proper

amount, the stopper may be inserted and the solution shaken, thus securing a thorough mixing.

74. Pipettes.—The pipette is generally used to transfer definite quantities of a solution from one vessel to another. The form shown in Fig. 11 is best adapted to this purpose and is the one most largely used. In using the pipette the lower end is placed in the solution, and the air is sucked out of the pipette by applying the lips to the upper end, thus causing the solution to rise and fill it. When the solution has reached a point somewhat above the mark, the finger, which should be slightly moist, is quickly slipped over the top of the pipette, thus keeping the air out and, consequently, keeping the solution in. As a rule, the solution will still stand a little above the mark on the stem, and the pipette should be revolved under the finger, thus allowing a little air to get in, until the column of liquid falls so that the bottom of the meniscus exactly coincides with the mark on the stem. Then, while pressing the finger firmly on the top of the burette, remove it to the vessel into which it is to be emptied, and lift the finger. Hold the pipette in a vertical position until the solution has run out and it has thoroughly drained; and then touch the tip to the damp side of the vessel, into which the solution was emptied, to remove the last drop, which always adheres to the tip of the pipette. In order to obtain uniform results when working with a pipette, the same method of using it must always be employed; and as the method just described gives the most consistent results, it is recommended. Beginners invariably find it difficult to handle the pipette quickly and accurately, and should practice filling it with water and emptying it until this becomes easy, before using it in handling solutions. Such practice may prevent painful injuries, caused by drawing acid or alkali solutions into the mouth.

FIG. 11.

A pipette is very often used in cases where a sample of a substance is dissolved and different parts of the solution are taken for different determinations. Thus, 5 grams of a substance may be dissolved in a 250-cubic-centimeter flask, and several portions of 50 cubic centimeters each may be withdrawn for the different determinations with a 50-cubic-centimeter pipette. As each of these portions contains one-fifth of the solution, it contains 1 gram of the sample. For this purpose, it is not necessary that the pipette should hold exactly 50 cubic centimeters, nor that the flask should hold exactly 250 cubic centimeters, but it is necessary that the flask should hold exactly five times as much as the pipette. Whether the pipette and flask are in perfect harmony or not may be learned by filling the pipette to the mark with water, and emptying it into the flask five times. If the bottom of the meniscus just comes to the mark on the neck of the flask, they agree, but if this fails, several more trials should be made and a new mark should be made on the flask before proceeding with the analysis. Pipettes are made in various sizes. Those holding 2, 10, 50, and 100 cubic centimeters are probably the most largely used.

FIG. 12.

75. Flasks.—In making up standard solutions, the exact measurements required cannot be made in a cylinder, for a slight addition of liquid will not raise the surface of the solution sufficiently, hence some other measuring vessel must be employed. Undoubtedly the most convenient vessel for this purpose is an accurately graduated flask, similar to the one shown in Fig. 12. These flasks should be as narrow in the neck as is compatible with convenience in use, for the smaller the neck of the flask, the more accurately the amount of solution present may be determined, but the neck should not be so narrow

as to cause inconvenience in introducing or withdrawing substances.

Measuring flasks should be made of well annealed glass, and should be rather thin, but of uniform thickness throughout, so that the danger of breaking by changes of temperature will be reduced to a minimum. They should be supplied with ground-glass stoppers, and the graduation marks should fall below the middle of the neck, so that the contents of the flask can be mixed by shaking. Graduated flasks are also largely used in dissolving substances and making the solution up to a certain volume before removing parts of it for different determinations with a pipette. In making up standard solutions, a flask having a capacity of 1 liter is most largely used. The other sizes most frequently used are those having capacities of 200, 250, 300, and 500 cubic centimeters.

76. Burettes.—The instrument from which the standard solution is measured into the solution to be analyzed is known as a burette. This instrument has been made in a variety of forms, but only a few of these are in use at the present time. Each of these consists of a graduated tube provided with some arrangement by which a solution may be allowed to flow from the burette, or its flow stopped at will. The simplest and cheapest form of burette is described and illustrated in Art. **118**, *Theoretical Chemistry*, and for many purposes this form is as good as any. It is sometimes modified by dispensing with the pinch cock, and introducing a glass ball or short piece of glass rod into the rubber tubing at the bottom of the burette. The ball or piece of rod must be just large enough to prevent any of the solution from passing through the tube when standing undisturbed. To draw off a portion of the solution from the burette, it is only necessary to pinch the rubber tube over the ball or piece of rod, with the fingers, thus forming a channel, past the side of the obstruction, through which the liquid can freely pass; and to immediately stop the flow of liquid it is only necessary to relax the fingers. Burettes of this form are very

handy for some purposes, but cannot be used in all cases, as the rubber decomposes some standard solutions, such as potassium permanganate and iodine.

When solutions which are decomposed by coming in contact with rubber are to be employed, a burette having a glass stop-cock, as shown in Fig. 13, must be used. This form of burette is so handy, and is now sold at such a moderate price, that it has largely displaced the older form just described. Before using the burette, the stop-cock should be coated with a thin layer of grease. Several kinds of grease have been recommended for this purpose. Both tallow and vaseline are good, but the writer prefers a mixture of beeswax and tallow. This burette may be so regulated as to deliver the solution at any desired rate, and may be used for all solutions. Owing to the action of alkalies upon glass, however, this form of burette, when used for strong alkalies, should be immediately emptied and washed after use, or the solution will not only be partially decomposed, but will attack the stop-cock, causing it to stick, and, in a short time, to leak. Of course, such a solution should not be allowed to stand in any burette, for, in addition to decomposing, it slowly dissolves the glass from the inside of the tube, thus rendering the graduation inaccurate.

FIG. 13.

All the ordinary forms of burette are graduated from the top to the bottom, so that, starting with the burette filled to the zero mark, the reading after adding the solution indicates the quantity of solution used in the operation. If the liquid does not stand at the zero mark at the beginning of the titration, the first reading of the burette subtracted from the second gives the quantity of solution used. A uniform method of reading the burette must be adopted. The bottom of the meniscus is usually chosen, but whether the top or bottom is chosen is a matter of little importance, so long as both readings are taken in the same manner. Taking the first reading at the top of the meniscus, and the

second at the bottom, or vice versa, would obviously introduce an error. As readings taken at the bottom of the meniscus are, in some cases, more uniform, this method is usually adopted; but, in the case of strongly colored solutions, it is difficult to see the bottom of the meniscus, and the readings in such cases are generally taken at the top.

The burette may be supported by any burette stand, or clamp, that will hold it in a vertical position. The second reading should not be taken as soon as the titration is completed, but a few seconds should be allowed for the drops of liquid adhering to the sides of the burette to run down and unite with the solution. In all readings, the burette should be in a vertical position, and the eye must be on a level with the top of the liquid. The part of the burette containing liquid should not be touched with the hand unless this is necessary, as the warmth thus imparted to the liquid may be sufficient to cause perceptible expansion. For the following determinations, two burettes will be required. For the work on acids and alkalies, any of the forms described may be used, but should be as nearly uniform in style and size as possible. For some of the other determinations a burette with a glass stop-cock will be required. Burettes having capacities of 50, 75, or 100 cubic centimeters are the handiest for general work.

ACIDIMETRY AND ALKALIMETRY.

77. That we may be able to determine the acidity or alkalinity of any solution, it is well to have on hand correct standard solutions of sodium carbonate, sodium hydrate, sulphuric acid, and hydrochloric acid. The practice obtained by the student in making up these solutions at the beginning of his work in volumetric analysis will be of great value to him.

Several methods of making up these solutions have been proposed by different chemists. Oxalic and sulphuric acids have been used as the starting point, but on account of the facts that perfectly pure sodium carbonate is easily obtained,

that the solution is readily made up, and is perfectly reliable, the solutions here described will be based upon sodium carbonate.

INDICATORS.

78. When an acid and an alkaline solution are mixed, there is nothing in the appearance of the mixture to indicate when the point of neutrality is reached; hence a substance known as an indicator must be added. We have seen that certain organic coloring matters exhibit one color in an alkaline solution, and a different color in solutions having an acid reaction, and this fact is made use of in working with acids and alkalies. A little of one of these coloring matters is added to the solution to be titrated, and the standard solution is added till the color changes. Litmus is probably the oldest and best known of the organic indicators, but some of the newer ones have largely displaced it at the present time. The two organic indicators which are probably most used at the present time, and are in many ways the best, are phenol-phthalein and methyl-orange.

79. Phenol-Phthalein.—Phenol-phthalein solutions having a good strength for use may be made by dissolving 1 gram of the powder in 500 cubic centimeters of 50-per-cent. alcohol. This is one of the most delicate of the indicators, and gives a very sharp reaction in all solutions to which it is suited. In neutral or acid solutions, this indicator is colorless, but the faintest excess of caustic alkali immediately imparts to it a bright-red color. It is not suited to solutions containing carbonates, free ammonia, or ammonium compounds, for in the presence of ammonia or carbon dioxide, the end reaction is not distinct, and the change of color does not indicate the exact point at which the reaction of the solution changes. It is one of the best, if not the best, of the indicators for solutions of the hydrates of the fixed alkalies, and for all acids, both inorganic and organic, except carbonic acid. The fact that it can be used in alcoholic solutions, or in mixtures of alcohol and ether, renders it useful in

determining organic acids which are insoluble in water. It may also be used in estimating the acids combined with many of the alkaloids.

80. Methyl-Orange.—A solution of methyl-orange, of convenient strength for use, is made by dissolving 1 gram of the powder in 1 liter of pure distilled water. It is cherry-red in an acid solution, and yellow in a solution having an alkaline reaction. This reagent cannot be used in estimating the organic acids, as they render the end reaction indefinite; but it is not affected by ammonia or carbon dioxide, hence it is especially useful in standardizing acids by means of sodium carbonate, and as an indicator in the presence of ammonia or its salts. The change of color is not so marked as in the case of phenol-phthalein, but it is very distinct if carefully handled. Too large a quantity of the indicator should not be used. Two or three drops of the solution described are sufficient for 100 cubic centimeters of solution. Nearly all of the organic indicators give a sharper reaction in cold than in hot solutions; hence, so far as possible, the solutions to be titrated should be cool. It will be noticed that either one or the other of these indicators can be used with all solutions likely to be met in acidimetry and alkalimetry.

PREPARATION OF SOLUTIONS.

81. It is possible to titrate all acid and alkali solutions with only one standard solution of each kind; but it frequently happens that acid and alkali solutions are used for other processes in which some particular solution is required; hence, it is well to make up several of the solutions most frequently used It is absolutely necessary, at all events, to have at least one acid and one alkali solution which are strictly accurate to serve as foundations in making up all others. On account of the ease with which a strictly accurate solution of sodium carbonate is obtained, this is the best alkali solution to serve as a basis for other solutions, but on account of its limited use for other purposes, at least one

other alkaline solution should be made up for use in general analytical work. For the standard normal acid, sulphuric acid is probably the best, as it is easy to obtain in a strictly pure condition, and the solution, if properly preserved, will retain its exact strength almost indefinitely. This cannot be said of any of the alkali solutions, for they all attack the glass to a greater or less extent, especially when hot, and dissolve some of the alkali contained in the glass. For this reason, a flask made of Jena glass—upon which this action is not nearly so great as upon ordinary glass—should be used in making up the solutions, and after standing for any considerable time, these solutions must be restandardized before they are used. They should be kept in bottles having ground-glass stoppers, and a little grease should be placed on the stopper to close the bottle still more tightly and, in the case of alkali solutions, to protect the glass from the solution.

82. Normal Sodium Carbonate.—As the molecular weight of sodium carbonate is 106, and the molecule contains 2 atoms of sodium, a normal solution contains 53 grams of the salt to the liter. To prepare it, heat rather more of the perfectly pure salt than will be required for the solution until all moisture is driven off. If a large platinum dish is available, this is best done by placing the salt in this dish and heating over a Bunsen burner until the dish assumes a dull-red color, keeping it at this temperature for 10 or 15 minutes and stirring occasionally with a platinum wire, but taking care not to fuse the salt. If a suitable platinum vessel is not at hand, the same object may be accomplished, if the salt is perfectly pure, by heating it in a clean porcelain dish. In either case, allow it to cool in a desiccator, and when quite cool, weigh out exactly 53 grams of it, with as little delay as possible. Place this in a rather large beaker and dissolve it in 300 or 400 cubic centimeters of water, which is quite hot, but not boiling. When this solution has cooled almost to the temperature of the room, transfer it to a graduated liter flask, and rinse out the beaker with successive small quantities

of water, adding each of these to the solution in the flask, and taking care not to spill any of this liquid, thus making sure that every particle of the sodium carbonate finds its way into the flask. Now dilute the solution exactly to the mark on the neck of the flask, insert the stopper, shake well to secure as thorough mixing as possible, then pour the solution into the perfectly dry bottle in which it is to be kept, stopper the bottle tightly, and shake again to secure thorough mixing. The temperature at which the solution is to be made up is marked on nearly all graduated flasks, and the solution and the water with which it is diluted should be at this temperature when it is made up to the liter, and the solution should be at the same temperature when used. The matter of temperature is quite important when working with normal solutions, for with such strong solutions, a change of a few degrees may introduce a perceptible error in the work.

If strictly pure sodium carbonate is not at hand, the bicarbonate, which is easily obtained in a pure state, may be used in making up this solution. In this case the bicarbonate is converted into normal carbonate by means of heat. 85 grams of the bicarbonate, when heated, yields slightly more than 53 grams of the normal carbonate, but a little more than this should usually be taken, as it frequently happens that it is difficult to remove all of the carbonate from the dish. To prepare the solution in this way, place the perfectly pure salt in a clean platinum dish, and heat to dull redness for 10 or 15 minutes, stirring from time to time with a platinum wire, and taking care not to fuse the salt. The bicarbonate is now converted into normal carbonate. Allow it to cool in a desiccator, weigh out 53 grams as quickly as possible, and dissolve it as previously described.

As much of the sodium carbonate of commerce contains bicarbonate, unless certain that the sample is free from bicarbonate, it should be heated in a platinum dish to convert any bicarbonate that may be present into normal carbonate. This solution should be prepared with the utmost care, for all the other solutions depend upon this one, and if this is wrong, all the others will be useless. As 1 liter of a normal

solution of sodium carbonate contains 53 grams of the salt, 1 cubic centimeter contains one-thousandth of this, or .053 gram of Na_2CO_3.

83. Normal Sulphuric Acid.—A normal solution of sulphuric acid contains 49 grams of the anhydrous acid to the liter, but as the pure acid cannot be weighed and diluted to a certain volume, some other method must be adopted, and, as has been indicated, the best method is to make up a rather strong solution, and dilute this until a certain volume of it exactly neutralizes an equal volume of the normal sodium carbonate. To do this, slowly pour about 30 cubic centimeters of pure sulphuric acid, of 1.84 specific gravity, into from 200 to 300 cubic centimeters of distilled water in a beaker, and, after this has cooled to the right temperature, transfer it to a liter cylinder and dilute to about 1 liter with water of the proper temperature. Then place the stopper in the cylinder, and shake well to secure a thorough mixing.

Fill one burette with normal sodium-carbonate solution and the other with the acid solution. From the burette containing sodium carbonate, measure exactly 10 cubic centimeters of solution into a beaker; dilute to about 100 cubic centimeters with pure water, add 2 or 3 drops of methyl-orange, and then, from the other burette, add the sulphuric acid, until the change of color of the indicator shows that the point of exact neutrality is reached. Repeat this operation once or twice, and take the mean of two or three readings—or even more, if these do not agree closely—as the amount of the acid required to neutralize 10 cubic centimeters of the sodium carbonate. From this, calculate how much water must be added to the acid, and dilute it accordingly. The calculation may be made by means of a simple proportion. For instance, if 9.5 cubic centimeters of the acid are required to neutralize 10 cubic centimeters of the sodium carbonate, and 950 cubic centimeters of the acid remain in the cylinder, the proportion would be $9.5 : 10 = 950 : x$. $x = 1{,}000$ cubic centimeters, or 1 liter. Hence, in order to make the sulphuric-acid solution of such

strength that equal volumes of the two solutions shall exactly neutralize each other, it is necessary to dilute the 950 cubic centimeters of solution in the cylinder to the liter mark with pure water.

In practice, it is very difficult to measure such large quantities of liquid with sufficient accuracy so that the solution can be diluted to exactly the required strength at once, unless it is very nearly of the proper strength to start with; and as it is much easier to dilute a solution which is too strong than to strengthen one which is too weak, it is best to add a few cubic centimeters less than the calculated amount of water; mix well, and make a second calculation by titrating a quantity of this freshly diluted acid in the same manner that it was done in the first instance. Before leaving the sulphuric-acid solution, 50 cubic centimeters of it should be made to exactly match 50 cubic centimeters of the sodium carbonate. As the strength of the sulphuric-acid solution is made to depend upon the sodium carbonate, the quantity of solution made up is not a matter of importance, and exact measurement of the whole volume of solution is not required, as the measurement in a cylinder is sufficiently accurate to show how much the solution should be diluted, provided this is done as directed. In cases where absolute accuracy is demanded, it is a good plan to check the strength of this solution by precipitating a portion of it with barium chloride, weighing the barium sulphate, and from this calculating the amount of sulphuric acid present. To do this, measure exactly 25 cubic centimeters of the solution into a beaker, by means of a burette; dilute this to 150 or 200 cubic centimeters with pure water, heat to boiling, and precipitate the sulphuric acid with a slight excess of barium chloride. Treat the precipitate of barium sulphate thus obtained exactly as described in Art. **66**, and from its weight calculate the amount of sulphuric acid in a liter of the solution. It has been the writer's experience that the results obtained by this method never necessitate any change in the strength of a solution which has been carefully standardized against a properly prepared solution of sodium

carbonate. One cubic centimeter of a normal solution of sulphuric acid contains .049 gram of H_2SO_4.

84. Normal Sodium Hydrate.—A normal solution of sodium hydrate contains 40 grams of the salt per liter; but, as the solid attracts moisture so rapidly, it cannot be weighed accurately, and consequently a solution having approximately the proper strength must be made up, and this must be standardized against the normal acid. To make this solution, weigh out 45 or 50 grams of the pure sodium hydrate, dissolve it in distilled water, and dilute the solution to about 1 liter. This is probably best done by placing the solid in a liter cylinder, adding about a liter of water, and agitating so that the heat generated during solution will not break the cylinder; or it may be dissolved in a beaker, and then transferred to the cylinder. When all is dissolved, standardize the solution against the sulphuric acid in the same manner that the sulphuric acid was standardized against the sodium carbonate. As no carbon dioxide is present in this case, phenolphthalein gives a more distinct end reaction than methyl-orange, hence its use is recommended; but it is best to make duplicate titrations, using methyl-orange as the indicator, as a check. In this, as in every case, the solution should be allowed to cool to the proper temperature before it is standardized. As sodium hydrate of this strength absorbs carbon dioxide quite rapidly, it should be protected from the air as much as possible while being used, and should be kept in a tightly stoppered bottle, which is nearly filled by the solution. One cubic centimeter of normal sodium hydrate contains .04 gram of $NaOH$.

85. Normal Hydrochloric Acid.—A normal solution of hydrochloric acid contains 36.37 grams of HCl to the liter. To prepare it, make a solution rather stronger than normal, titrate this against the normal sodium hydrate, using phenolphthalein as the indicator, and dilute this solution until 50 cubic centimeters of it exactly neutralize 50 cubic centimeters of the sodium hydrate, in the same way that the

sulphuric acid was standardized against the sodium carbonate. This solution will not retain its exact strength as well as the sulphuric-acid solution, but it has the advantage that it does not form insoluble compounds with the alkaline earths, and consequently may be used to titrate solutions containing these metals.

The strength of this solution may be verified gravimetrically, as in the case of sulphuric acid. To do this, measure exactly 15 or 20 cubic centimeters of the solution into a beaker, by means of a burette, dilute to about 100 cubic centimeters with cold water, and precipitate the chlorine, at the temperature of the room, with a slight, but sure, excess of silver nitrate, to which a little nitric acid has been added. When an excess of silver nitrate has been added, gradually heat the solution almost to boiling, while stirring it continuously, thus causing the precipitate to collect and settle. Treat the precipitate as directed in Art. **12**, and from its weight calculate the amount of hydrochloric acid in the solution. One cubic centimeter of a normal solution of hydrochloric acid contains .03637 gram of HCl.

86. Verification of Solutions.—As in this scheme for the preparation of solutions, the strength of each solution is made to depend upon the one standardized just previously, if 25 cubic centimeters of the hydrochloric acid exactly neutralize 25 cubic centimeters of the sodium carbonate, it is a strong indication that all the solutions are correct, but before they are accepted, they should be tested to prove that each of the acids exactly matches each of the alkali solutions. In doing this, it must be remembered that whenever a carbonate solution is titrated, methyl-orange must be used as the indicator. In addition to testing these solutions against each other, the hydrochloric-acid and sulphuric-acid solutions may be tested gravimetrically as described under each of these acids.

87. Decinormal Solutions.—Normal solutions are too strong to be used in making accurate determinations of small quantities of substances or in titrating very dilute solutions,

and for these purposes solutions one-tenth as strong as the normal ones are made up. These are known as decinormal solutions, and are generally written $\frac{n}{10}$. By this arrangement, the same relationship is maintained between the solutions, and the factors are the same, except that the decimal point is moved one place further to the left. These solutions may be made by dissolving 5.3 grams of sodium carbonate in water, making it up to exactly 1 liter, and using this as a foundation for the others, as in the case of the normal solutions; or 100 cubic centimeters of each of the normal solutions may be accurately measured into flasks and diluted to exactly 1 liter. These solutions may be standardized against the normal solutions. Ten cubic centimeters of normal solution will, of course, require 100 cubic centimeters of decinormal solution for saturation. This method of standardizing is not advised, as a very slight error in measuring out the normal solution causes ten times as great an error in the decinormal one. As a rule, greater accuracy is obtained by carefully measuring out 100 cubic centimeters of normal solution and diluting to an exact liter, or basing all the solutions on a carefully prepared sodium-carbonate solution. Whatever method is employed in the preparation of these solutions, they must be made to agree perfectly among themselves.

USE OF NORMAL ACID AND ALKALI SOLUTIONS.

88. On account of their convenience, these solutions are largely used in laboratories connected with the soap, alkali, and paper industries. One of the chief advantages of these solutions is that, as they are all matched, we can tell the exact amount of any alkali in a solution by any acid, and vice versa, and the calculation is very simple. For instance, if we find that 50 cubic centimeters of a sodium-hydrate solution require 10 cubic centimeters of normal acid for saturation, we know that the solution contains as much sodium hydrate as would be contained in 10 cubic centimeters of a normal solution. As 1 cubic centimeter of

normal solution contains .04 gram of $NaOH$, 10 cubic centimeters contain .4 gram. Therefore, the 50 cubic centimeters of solution for analysis contain .4 gram of $NaOH$. In any case, it is only necessary to calculate the weight of a substance that would be contained in 1 cubic centimeter of a normal solution from the molecular weight of the substance, and multiply this factor by the number of cubic centimeters of normal solution required to saturate it. Only a few determinations in which these solutions are applied in practice will be described, but if the student performs these carefully, he will have no trouble with other applications.

89. Determination of Sodium Carbonate.—Weigh out accurately from 1 to 2 grams of pure, dry sodium carbonate; transfer it to a beaker, and dissolve in from 100 to 150 cubic centimeters of warm water. When the solution has cooled, add 3 or 4 drops of methyl-orange, and titrate with one of the normal acid solutions. As 1 cubic centimeter of a normal acid neutralizes .053 gram of sodium carbonate, the number of cubic centimeters of normal acid used multiplied by .053 will give the weight of the sodium carbonate. As the pure, dry salt was taken for analysis, the weight obtained by titration should coincide with the weight of sample taken, and this method is often used to verify the strength of normal acid solutions. This determination may be varied by weighing out 2 or 3 grams of crystallized sodium carbonate $Na_2CO_3, 10H_2O$, and treating it in the same manner as the dry sodium carbonate. In this case a slight calculation will be required, and if the accuracy of the work is to be checked by calculation, pure crystals which have not lost water must be taken.

90. Determination of Ammonium.—A method for the determination of ammonium, which is applicable in all cases where no nitrogenous organic matters from which ammonia might be evolved are present with the ammonium salts, is based upon the expulsion of ammonia by means of sodium hydrate, absorbing the ammonia thus set free in normal acid, and titrating the excess of acid with normal

alkali. To accomplish this, tightly fit a flask *A*, Fig. 14, having a capacity of about 250 cubic centimeters, with a perforated rubber stopper. Through the perforation in the stopper, pass a bent glass tube and, by means of a tightly fitting rubber tube or a strip of pure rubber, connect this tube with the condenser *B*, taking care that the ends of the two glass tubes are brought close together and that the connection is perfectly tight. Connect the lower end of the condenser with another tube in the same manner, and pass this tube through the perforation of a rubber stopper which is tightly fitted into the neck of the tubulated receiver *C*. Fit the tubulure of the receiver with a perforated rubber stopper, and by means of a glass tube passing through this, and bent twice at right angles, connect the receiver with the bulbed **U** tube *D*, in such a manner that the **U** tube stands in an upright position. Care must be taken to have all the connections perfectly tight. If a condenser is at hand, the inner tube of which extends some distance past the jacket tube at each end, the upper end may be bent, and connected with the flask, and the lower end may be inserted through the stopper into the condenser, thus dispensing with two connections.

Remove the stopper from the flask *A*, and introduce about 100 cubic centimeters of sodium-hydrate solution. The exact strength of this solution is not a matter of importance, but one a little stronger than normal (about 1.06 Sp. Gr.) is most satisfactory. Place a burner under this and bring it to boiling for a few moments, to expel any ammonia that the solution may contain. Allow this to cool, and while cooling, measure exactly 50 cubic centimeters of acid in a burette; introduce enough of this into the **U** tube to fill the lower bulb, and place the rest in the receiver. Great care must be taken in introducing the acid not to lose a particle of it, and to get exactly 50 cubic centimeters into the **U** tube and receiver. The acid used is not a matter of great importance, but sulphuric acid is generally preferred. The end of the tube leading from the condenser should be so arranged that it comes near the surface of the acid, but does not dip into the acid at any time in the process.

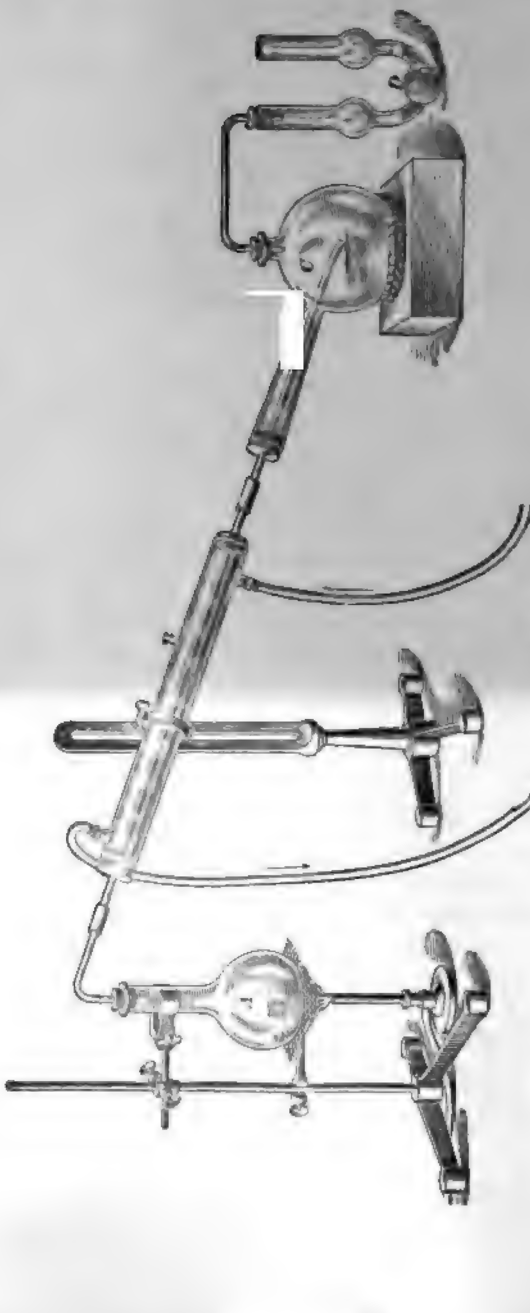

FIG. 14.

Into a short but wide tube, that is closed at one end (a test tube cut off about 1½ inches from the bottom serves well), weigh, accurately, about 1 gram of pure, dry ammonium chloride or such a quantity of other ammonium compound as would contain about the same weight of ammonium as 1 gram of the chloride. When the sodium-hydrate solution has cooled, drop this tube of sample into it, and quickly close the connection. Now bring a burner under the flask, which should be standing upon a wire gauze, and apply a regular amount of heat until about half of the liquid has slowly distilled over. If a double compound of ammonium is taken for analysis, the distillation may be attended by considerable bumping. Though comparatively rigid, the apparatus may be given a a slight motion, which, if constantly kept up, will cause sufficient motion in the liquid to prevent disturbance. When the distillation is complete, remove the stopper from the flask, turn out the burner, and allow the liquid to cool for 20 minutes. Disconnect the apparatus, pour the contents of the receiver and **U** tube into a beaker, and rinse these vessels till they are perfectly clean, with small successive quantities of pure water. To the solution in the beaker, add a few drops of methyl-orange as indicator, and determine the amount of acid which is still free, by titration with normal alkali. In this way the amount of acid neutralized by the ammonia is obtained, and from this result the amount of ammonium which was contained in the salt, and was expelled by the hot sodium hydrate in the form of NH_3, is calculated.

This calculation is quite simple. The number of cubic centimeters of normal alkali required to neutralize the acid subtracted from 50—the number of cubic centimeters of acid taken—gives the number of cubic centimeters of normal acid neutralized by the ammonia. This result multiplied by .049 gives the weight of sulphuric acid neutralized, and from this the weight of ammonium is calculated by the proportion:

$$H_2SO_4 : 2NH_4 = \text{wt. of } H_2SO_4 : x.$$

The weight of NH_4 thus obtained divided by the weight of sample taken and this result multiplied by 100, gives the per cent. of ammonium in the sample.

The acid also tends to prevent oxidation. As soon as the salt is all in solution, dilute it to about 200 or 250 cubic centimeters with cold water and titrate at once with permanganate in the same way that is done in standardizing. As in this case, exactly 1 gram of sample was taken for analysis, the number of cubic centimeters of permanganate used, gives the percentage of iron in the sample. If the burette was filled to the zero mark to start with, the percentage of iron may be read directly from the burette.

It is not necessary to take just 1 gram of sample for analysis. In fact, when working with these salts which only contain a small percentage of iron, it is better to use a sample weighing from 1.5 to 2 grams. The weight of iron in the sample is then obtained by multiplying the number of cubic centimeters of permanganate used by .01, and the percentage is obtained from this in the usual manner.

96. Determination of Iron in Ferric Compounds. Weigh a suitable quantity of some soluble ferric compound—2 grams of iron alum $FeNH_4 2SO_4, 12H_2O$ or an equivalent quantity of other weighable ferric compound serves well—and dissolve it in about 50 cubic centimeters of water in a flask having a capacity of about 250 cubic centimeters. To this solution add about 20 cubic centimeters of concentrate sulphuric acid and 10 grams of granulated zinc which is free from iron, and heat sufficiently to cause the acid to act rapidly on the zinc. A small funnel should be placed in the mouth of the flask to catch any particles of iron solution which would otherwise be spattered out of the flask and lost, and to help keep air out of the flask. The nascent hydrogen produced by the action of the acid on the zinc, reduces the iron quite rapidly, and in 15 or 20 minutes all should be reduced to the ferrous state.

While the reduction is going on, fold a large filter as shown in Fig. 15, and fit it into a large funnel. When reduction is complete, pour the contents of the flask into this filter. Add about 100 cubic centimeters of cold water and 5 cubic centimeters of sulphuric acid to the flask, shake

to determine the chlorine in any soluble chloride. As sodium chloride is easily obtained in a pure state, and is a handy salt to work with in other ways, it is a good one to use for practice.

Weigh out from .2 to .3 gram of pure, dry sodium chloride, and dissolve it in about 60 cubic centimeters of water, in a beaker. Care should be taken that this solution shall have as nearly as possible the same volume as the solution used in standardizing the silver solution. Add 2 or 3 drops of potassium-chromate solution, and titrate with the silver nitrate in the same manner that the titration was performed in standardizing the solution, taking care to add the standard solution until the same shade of red is obtained in the solution that was produced when standardizing. The number of cubic centimeters of solution used multiplied by the decinormal factor for chlorine (.003537) gives the weight of chlorine in the sample, and from this the percentage is obtained in the usual manner.

As silver chromate is soluble in both acids and alkalies, the solution in which chlorine is determined by this method must be neutral or very nearly so. If strongly alkaline, it should be nearly neutralized with pure nitric acid before titration, and if acid, it should be neutralized with sodium carbonate. As it is better to have the solution slightly alkaline than acid, it is best to add a very slight excess of sodium carbonate when neutralizing with this reagent. Sodium salts interfere with the reaction less than ammonium or potassium compounds, hence sodium carbonate should always be used in neutralizing an acid solution for this purpose. If too much of the silver solution should be added, this may be remedied by adding 1 cubic centimeter of decinormal sodium chloride, titrating again with silver nitrate, and subtracting 1 cubic centimeter from the total amount of silver-nitrate solution used.

IRON.

93. There are several methods of determining iron volumetrically, but only two of these are used to any considerable extent. Both of these methods depend upon the oxidation

of iron from the ferrous to the ferric state, by means of solutions having a known power of action. In either case, if the iron is originally in the ferric condition, it must be reduced to the ferrous state before titration. In one of these methods, potassium permanganate is used as the oxidizing agent, and in the other, potassium bichromate is employed as the standard solution. The permanganate method is the easier to perform, and the end reaction is the clearer, hence it is preferred in all cases in which it is applicable, but in the presence of hydrochloric acid this solution can only be used when special precautions are taken, which render the method unsatisfactory in any but experienced hands; hence, in the presence of hydrochloric acid, the bichromate method is usually employed.

THE PERMANGANATE METHOD.

94. Preparation of the Permanganate Solution.—As a permanganate solution is very largely used in the determination of iron, it is very handy to have the solution of such strength that when 1 gram of sample is taken for analysis, the reading of the burette in cubic centimeters gives the percentage of iron in the sample directly, thus avoiding the necessity of a calculation. To prepare such a solution, dissolve about 6 grams of pure potassium permanganate in water in a liter cylinder, and dilute it nearly to a liter. Then weigh out accurately 2 portions of perfectly pure ferrous ammonium sulphate $Fe(NH_4)_2 2SO_4, 6H_2O$, weighing, respectively, .7 and 1.4 grams. Place these samples in beakers; add about 50 cubic centimeters of water and 15 cubic centimeters of concentrate sulphuric acid to each, and bring into solution as rapidly and with as little exposure to the air as possible. As soon as solution is complete, dilute each sample to 150 or 200 cubic centimeters with cold water, and titrate each solution with the permanganate, carrying the whole operation through as rapidly as possible, to avoid oxidation of the iron, by action of the air. The solution should be stirred continuously during the

titration. As the permanganate falls into the ferrous solution, it is rapidly decolorized so long as the solution contains ferrous iron. As the end of the reaction is approached the color disappears less rapidly, and finally an additional drop of the permanganate imparts a permanent pink color to the solution, indicating that the reaction is complete. Note the volume of solution used, and then titrate the second sample in the same manner. From these results, calculate how much the solution must be diluted so that 1 cubic centimeter of it oxidizes .01 gram of iron, and dilute accordingly.

As ferrous ammonium sulphate contains exactly one-seventh its weight of metallic iron, the sample weighing .7 gram contains .1 gram of iron, and should therefore require 10 cubic centimeters of permanganate solution to oxidize it; and the sample weighing 1.4 grams should require 20 cubic centimeters. After dilution, the solution must be tested again in the same manner before it is used, in order to be certain that it is strictly correct. As the solution is now of such strength that 1 cubic centimeter of it oxidizes .01 gram of iron, each cubic centimeter used represents 1 per cent. of iron when exactly 1 gram of sample is taken for analysis. The reaction is

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4$$
$$= 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$$

Of course, it is not necessary in using this solution to take exactly 1 gram of sample. Any weight may be taken, and the weight of iron found by multiplying the number of cubic centimeters of solution used by .01. From this the percentage of iron may be obtained in the usual manner.

95. Determination of Iron in Ferrous Compounds.—Weigh exactly 1 gram of ferrous ammonium sulphate, ferrous sulphate, or some other weighable ferrous salt into a beaker; add about 50 cubic centimeters of water and 15 cubic centimeters of concentrate sulphuric acid and bring into solution with as little delay and exposure to the air as possible. The acid should be added immediately after the water, as otherwise a basic iron salt is likely to separate.

The acid also tends to prevent oxidation. As soon as the salt is all in solution, dilute it to about 200 or 250 cubic centimeters with cold water and titrate at once with permanganate in the same way that is done in standardizing. As in this case, exactly 1 gram of sample was taken for analysis, the number of cubic centimeters of permanganate used, gives the percentage of iron in the sample. If the burette was filled to the zero mark to start with, the percentage of iron may be read directly from the burette.

It is not necessary to take just 1 gram of sample for analysis. In fact, when working with these salts which only contain a small percentage of iron, it is better to use a sample weighing from 1.5 to 2 grams. The weight of iron in the sample is then obtained by multiplying the number of cubic centimeters of permanganate used by .01, and the percentage is obtained from this in the usual manner.

96. Determination of Iron in Ferric Compounds. Weigh a suitable quantity of some soluble ferric compound—2 grams of iron alum $FeNH_4 2SO_4, 12H_2O$ or an equivalent quantity of other weighable ferric compound serves well—and dissolve it in about 50 cubic centimeters of water in a flask having a capacity of about 250 cubic centimeters. To this solution add about 20 cubic centimeters of concentrate sulphuric acid and 10 grams of granulated zinc which is free from iron, and heat sufficiently to cause the acid to act rapidly on the zinc. A small funnel should be placed in the mouth of the flask to catch any particles of iron solution which would otherwise be spattered out of the flask and lost, and to help keep air out of the flask. The nascent hydrogen produced by the action of the acid on the zinc, reduces the iron quite rapidly, and in 15 or 20 minutes all should be reduced to the ferrous state.

While the reduction is going on, fold a large filter as shown in Fig. 15, and fit it into a large funnel. When reduction is complete, pour the contents of the flask into this filter. Add about 100 cubic centimeters of cold water and 5 cubic centimeters of sulphuric acid to the flask, shake

it around to rinse the flask, and as soon as the liquid has run through the filter, pour this on to the filter, thus rapidly washing out any iron that may remain in the paper. The funnel which was placed in the mouth of the flask during reduction should also be rinsed with this water as it is poured into the flask. Wash the flask and filter once more with cold water, and then titrate at once with permanganate. The calculation, of course, is the same as in the last instance.

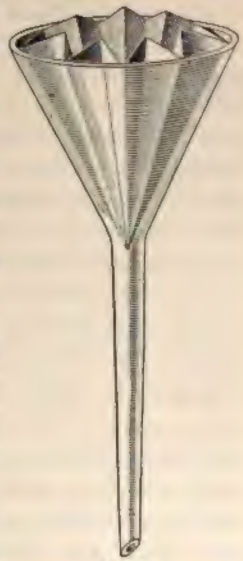
FIG. 15.

Most chemists advise allowing the solution to stand until the zinc is entirely consumed by the acid, replenishing the acid, if necessary, and then titrating without filtering, thus avoiding the necessary exposure of the liquid to air during filtration. It is the writer's experience, however, that equally accurate results are obtained when the solution is filtered, that much time is saved in this way, and the danger of getting particles of zinc into the solution is thus avoided. If any zinc is in the solution—which must be strongly acid—during titration, the nascent hydrogen thus generated decolorizes the permanganate rapidly, and to almost an indefinite extent, thus rendering titration impossible. The student is advised to try both of these methods of treating the reduced solution, and to note the one which he prefers, for this is one of the determinations frequently met in analytical work.

THE BICHROMATE METHOD.

97. Preparation of the Bichromate Solution.—Like the permanganate, the bichromate solution is generally made up so that 1 cubic centimeter of it oxidizes .01 gram of iron. The reaction of this case is

$$6FeCl_2 + K_2Cr_2O_7 + 14HCl$$
$$= 6FeCl_3 + 2KCl + 2CrCl_3 + 7H_2O$$

Hence, a solution, 1 cubic centimeter of which will oxidize .01 gram of iron, contains approximately 8.8 grams of potassium bichromate to the liter. To make this solution, dissolve from 8.8 to 9 grams of pure potassium bichromate in somewhat less than a liter of water, in a graduated liter cylinder, and shake the solution well to secure thorough mixing. Now make up a ferrous solution by dissolving .7 or 1.4 grams of pure fe[illegible] ammonium sulphate in about 50 cubic centimeters of water [illegible]d 10 cubic centimeters of concentrate sulphuric acid, [illegible] dilute to about 200 cubic centimeters with cold water. [illegible]o this ferrous solution, add bichromate from a burette un[illegible]l the iron is just oxidized completely. From the volume of bichromate required for this, calculate how much the solution must be diluted, and add water accordingly. The full calculated amount of water should not be added at once, however; but a few cubic centimeters less than the calculated amount should first be added and the solution again titrated. From the result obtained by this titration, the solution may be diluted to the proper strength, but it should not be accepted as correct until it has been tested by titrating another ferrous solution in the same manner.

There is nothing in the appearance of the solution to show when the reaction is complete, hence some other means of determining this must be adopted. For this purpose, place several drops of a solution of potassium ferricyanide, which has been freshly prepared from the very purest materials, on different parts of a clean porcelain plate. When it is thought that nearly enough bichromate has been added to oxidize the iron, stir the solution well, and remove a drop of it on the end of the stirring rod. Place this on the plate beside a drop of the ferricyanide, and by tipping the plate, bring the two drops in contact with each other. If a blue precipitate or coloration is formed, it shows that the solution contains iron which is in the ferrous condition, and, consequently that the reaction is not complete. Add a few drops more of

the bichromate, stir the solution well, and bring a drop of it in contact with another drop of ferricyanide on the porcelain plate. Continue this treatment until complete oxidation is obtained. As the end of the reaction is approached, the blue color grows fainter, and finally a point is reached at which a blue color is not imparted to the drop of test solution immediately, but will appear after standing a few moments. At this point, 1 or, at most, 2 more drops of the bichromate will usually be sufficient to complete the reaction. When complete, no blue color will be imparted to the test reagent, but a yellowish coloration will be produced. The exact point at which this reaction is complete may be rather difficult to recognize at first, but after a little practice it becomes quite easy, and the student is advised to make himself familiar with this process, as it is very often used in practical analytical work.

As potassium bichromate is a weighable salt, if a perfectly pure sample is at hand, the above method of standardizing the solution is not necessary, for the exact amount of bichromate may be weighed up, dissolved, and made up to an exact liter. If this method is employed, place some pure potassium bichromate in a porcelain or platinum dish and heat it till certain that all moisture is driven off. It is generally advised to heat the salt until it commences to fuse, but some chemists prefer to heat in the air bath at 110° until perfectly dry. For this purpose either method may be employed. When dry, cool the salt in a desiccator, weigh out exactly 8.7863 grams, dissolve it in pure water, and make up to exactly 1 liter in a graduated flask. If perfectly pure potassium bichromate is used, 1 cubic centimeter of this solution will oxidize .01 gram of iron; but to avoid the possibility of an error in the strength of the solution, due to impurity in the salt, when the solution is made in this way, it should always be tested against a ferrous solution of known strength before it is used.

98. Determination of Iron in Ferrous Compounds. Weigh out 1 or 2 grams of a perfectly pure dry sample of

some soluble ferrous compound which admits of exact weighing, place it in a beaker, and dissolve it in from 50 to 100 cubic centimeters of water and 10 cubic centimeters of concentrate sulphuric or hydrochloric acid, completing the solution as rapidly and with as little exposure to air as possible. Probably sulphuric acid is better than hydrochloric for this purpose, for solutions containing it do not appear to be acted upon by the air so rapidly as those acidified by hydrochloric acid. So far as the titration is concerned, however, there is probably no difference, or if there is any difference, it is in favor of hydrochloric acid. As soon as all the salt is in solution, dilute to 200 or 250 cubic centimeters and titrate it with the bichromate in the same way that this was done in standardizing the solution. If exactly 1 gram of sample was taken for analysis, the number of cubic centimeters of solution used, gives the percentage of iron in the sample directly. If any other weight of sample was taken, the number of cubic centimeters of solution used divided by this weight gives the percentage of iron. In working with this solution, it is always best to dissolve two portions of the sample. To one of these add the bichromate, 5 cubic centimeters at a time, until it is thought that the point of complete oxidation is nearly reached; then add the solution, 1 cubic centimeter at a time, stirring well and testing after each addition of standard solution. In this way, the approximate amount of bichromate solution required is learned from the first sample. Now, to the second sample, add nearly the required volume of bichromate solution at once, and then complete the titration very cautiously. By using one solution in this way to learn the approximate volume of bichromate required, much time is saved, and the results obtained are probably more accurate, as the solution suffers less exposure to the air.

99. Determination of Iron in Piano Wire.—Weigh out from .3 to .5 gram of bright, clean piano wire, and place it in a rather small beaker. Add about 5 cubic centimeters of water, then from 15 to 20 cubic centimeters of concentrate

hydrochloric acid; cover the beaker with a watch glass and heat till the wire is completely dissolved. Dilute this solution with an equal volume of water, and bring it to boiling. To the gently boiling solution, slowly add a solution of stannous chloride from a pipette or burette, until the color of the solution becomes very light. Then add to the solution 1 or 2 drops at a time, pausing a moment after each addition, and continue this treatment until the solution becomes perfectly colorless. Then add from 1 to 4 drops of solution—depending upon its strength—to make sure that all iron is reduced, but avoiding any considerable excess. Wash this reduced solution into a larger beaker and dilute it to 200 or 250 cubic centimeters with cold water, rinsing out the small beaker with this water. To this solution, add 15 cubic centimeters of mercuric-chloride solution all at once; stir well, allow to stand 1 minute, and then titrate with the bichromate solution. The number of cubic centimeters of bichromate solution used, divided by the weight of sample taken, gives the percentage of iron in the sample. Piano wire usually contains about 99.6 per cent. of pure iron.

The stannous-chloride solution is made up in different ways and of various strengths. A dilute solution is generally advised by the authors of works on chemistry, but a much stronger solution is generally employed in technical laboratories. Two methods of making up this solution are here given. The first is the solution usually recommended in chemical works, and the second is one largely used in iron and steel works' laboratories.

1. Weigh 12 grams of pure metallic tin into a porcelain dish, add a piece of platinum foil, then cover the tin with 200 cubic centimeters of concentrate hydrochloric acid, and heat till all is dissolved. Remove the platinum foil, dilute to 1 liter, and keep in a tightly stoppered bottle containing some metallic tin.

2. Weigh 100 grams of stannous chloride into a porcelain dish, add 100 cubic centimeters of concentrate hydrochloric acid, 300 cubic centimeters of water, and a little metallic tin, and boil till the solution is clear and colorless. Dilute the

solution to 500 cubic centimeters with a solution of 1 part of hydrochloric acid and 3 parts of water, and keep in a tightly stoppered bottle containing metallic tin.

Many chemists prefer a more strongly acid solution, and some dissolve the stannous chloride in a solution containing equal parts of concentrate hydrochloric acid and water.

The reaction which takes place, when one of these stannous solutions is added to a ferric solution, is

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4$$

and any of the above solutions will produce this reaction. A strong solution accomplishes this reduction most rapidly, but unless considerable care is exercised there is danger of getting too great an excess of stannous chloride in the iron solution. With a dilute stannous solution, this is more easily regulated, as a few drops more or less do not make a great difference; but this dilute solution reduces the iron much more slowly. For these reasons, two solutions are sometimes used. In this case, a strong solution is added until the color of the iron solution is almost destroyed, and the reduction is then completed, using the dilute solution; but if proper care is taken the reduction may be satisfactorily accomplished with one solution. A slight excess of stannous chloride must be added to the solution to make sure that the iron is completely reduced, but if this excess were left in the solution, it would reduce some of the bichromate and render the results inaccurate. A small amount of stannous solution may be rendered harmless by adding an excess of mercuric-chloride solution, if the conditions are right. In order that this shall succeed, the solution must be cool, must not contain a large amount of tin, and the mercuric-chloride solution must be added quickly, or all at once. The reaction produced in this case is

$$SnCl_2 + 2HgCl_2 = SnCl_4 + Hg_2Cl_2$$

and the success of the reaction is indicated by a white silky precipitate. If too much tin is present, if the solution is hot, or if the mercuric solution is added slowly, gray metallic mercury separates and interferes with the reaction when th

bichromate is added. If no precipitate is formed when the mercuric solution is added, it shows that no stannous chloride is present, and, consequently, that reduction is probably not complete; hence, a white silky precipitate should be obtained at this point, before the results obtained are accepted as correct. A saturated solution of mercuric chloride is used for this purpose, and the solution should always contain some of the undissolved salt. The potassium-ferricyanide solution, used as indicator, must be perfectly pure, and must be freshly prepared when wanted, as it is partially converted into ferrocyanide upon standing.

CALCIUM.

100. Determination of Calcium by Potassium Permanganate.—As we have already seen, there is no very satisfactory gravimetric method for the determination of calcium when a blast lamp and platinum crucible are not available; hence, the following volumetric method, which yields very accurate results when properly executed, is very handy in many cases. It is carried out as follows: Weigh out, accurately, about .5 gram of pure, dry calcium carbonate; place it in a beaker of rather deep form, cover the beaker with a watch glass, and dissolve the sample in a slight excess of hydrochloric acid, sliding the watch glass a little to one side while adding the acid. Apply gentle heat to complete the solution, if necessary. When solution is complete, dilute to about 100 cubic centimeters with water, and add 10 or 15 cubic centimeters of concentrate ammonia. If this causes a precipitate, dissolve it in concentrate hydrochloric acid, and again render the solution strongly alkaline with ammonia. The ammonium chloride formed when the precipitate is dissolved in hydrochloric acid will now keep the calcium in solution. Heat the solution to boiling and precipitate the calcium with a slight, but distinct, excess of ammonium oxalate, adding the reagent slowly and with constant stirring. Continue the boiling for a few moments, and then stand the beaker and contents in a warm place for

4 hours, for the precipitate to collect and settle, taking care that the solution remains strongly alkaline throughout the operation.

Decant the clear liquid through a filter, leaving the precipitate undisturbed. Add about 100 cubic centimeters of water and 2 or 3 cubic centimeters of ammonia, heat to boiling, and again allow the precipitate to subside. Now bring the precipitate on to the filter through which the solution was decanted, and wash with hot water containing a little ammonia, until all ammonium oxalate is washed out. Then wash twice with pure hot water, which has been recently distilled or has just been boiled. Place a rather large clean beaker under the funnel, break the apex of the filter with a glass rod, and wash as much as convenient of the precipitate into the beaker with water. Then wash the rest of the precipitate from the filter with hot dilute sulphuric acid, allowing these washings to run into the beaker with the precipitate. A solution of 1 part of acid to 4 parts of water is probably the best strength to use for this purpose. At least 150 cubic centimeters of acid solution should be used in washing the filter, and more may be used if necessary. It should be washed, at all events, until every particle of precipitate is removed to the beaker. Now dilute the solution to about 500 cubic centimeters, and heat to 70° or 80°, while stirring from time to time. The precipitate will usually be entirely, or nearly, dissolved at this point, and probably most of the calcium has been changed to sulphate and the oxalic acid set free. While the solution is at this temperature, titrate it with permanganate, adding this solution as rapidly as possible, to prevent its expansion in the burette, due to the heat from the calcium solution. The reaction is complete when the solution assumes a permanent pink tint. From the volume of permanganate used, the weight or percentage of calcium oxide CaO is readily obtained, and from this the weight or percentage of calcium can readily be calculated if it is wanted. A permanganate solution, standardized for the determination of iron, is peculiarly adapted to the determination of calcium oxide, on account of the relation of the

atomic weights. The action of the permanganate and sulphuric acid on the calcium oxalate may be expressed in one equation, as follows:

$$2KMnO_4 + 5CaC_2O_4 + 8H_2SO_4$$
$$= 5CaSO_4 + 2MnSO_4 + K_2SO_4 + 8H_2O + 10CO_2$$

Thus we see that 2 molecules of potassium permanganate, which oxidize 10 atoms of iron, oxidize 5 atoms of calcium, or, more correctly, 5 molecules of oxalic acid with which the calcium is united. As the molecular weight of calcium oxide and the atomic weight of iron are the same, it is evident from the above equation that a certain volume of potassium permanganate represents just half as much calcium oxide, by weight, as it does iron. Hence, 1 cubic centimeter of a permanganate solution which is equal to .01 gram of iron, is equal to .005 gram of calcium oxide. If exactly 1 gram of sample is taken, the percentage of CaO may be obtained by dividing the number of cubic centimeters of permanganate used by 2, provided the permanganate is of such strength that each cubic centimeter of it represents 1 per cent. of iron. If .5 gram of sample is taken, the number of cubic centimeters of permanganate used gives the percentage directly. Having obtained the weight or percentage of calcium oxide in this way, the percentage of calcium may be calculated by using the factor given in Art. **38**, which should be read in connection with this determination.

Instead of washing the precipitate off of the filter, many chemists prefer to place the precipitate and filter in a large beaker, covering them with hot dilute acid, and stirring well with a glass rod to break up the paper. Then dilute the solution, heat it to 70° or 80° and titrate with permanganate, as in the other case. It has been stated that the pieces of filter paper in the solution may have an action on the permanganate, but experience does not appear to justify this objection.

Dilute hydrochloric acid that does not contain free chlorine may be used to dissolve the precipitate, as there is no danger of chlorine being liberated in this case, but sulphuric acid is generally preferred for this purpose.

VOLHARD'S METHOD FOR CHLORINE, BROMINE, IODINE, SILVER, AND COPPER.

PREPARATION OF SOLUTIONS.

101. Ferric Indicator Solution.—A ferric solution is used as an indicator in this process. It is usually made by dissolving iron alum $FeNH_42SO_4,12H_2O$ in water until a saturated solution is obtained, and adding to this an equal volume of pure concentrate nitric acid that has recently been boiled to expel lower oxides of nitrogen.

102. Decinormal Silver Nitrate.—This solution contains 10.766 grams of metallic silver, or 16.966 grams of silver nitrate, in a liter. To prepare it, weigh exactly 5.383 grams of pure metallic silver into a graduated 500-cubic-centimeter flask, and dissolve it in pure nitric acid of about 1.2 specific gravity. A mixture of equal parts of concentrate acid and water serves well for this purpose. Boil this solution to expel any nitrous acid that may be present, allow it to cool, dilute to exactly 500 cubic centimeters, and shake well to secure thorough mixing. If pure metallic silver is not at hand, a decinormal silver-nitrate solution may be made up, as directed in Art. **91**, or exactly 8.483 grams of pure silver nitrate, which has been heated to 120°, and cooled in a desiccator before weighing, may be dissolved in water and made up to exactly 500 cubic centimeters in a graduated flask.

103. Decinormal Ammonium Sulphocyanide.—As this salt is quite deliquescent, a solution cannot be made by weighing up a definite quantity of the salt and diluting to the proper volume, hence an approximate solution must be made up and standardized against a correct decinormal silver solution. To make this solution, weigh out 4.2 or 4.3 grams of the fairly dry, pure ammonium sulphocyanide, dissolve it in water in a liter cylinder, dilute to about 500 cubic centimeters, and shake well to secure thorough mixing. From a burette, measure exactly 10 cubic centimeters of the

silver solution into a beaker, add 10 cubic centimeters of the ferric indicator, and dilute to 100 cubic centimeters. Now from another burette add sulphocyanide solution, until the last drop imparts a permanent red color to the solution. Repeat this titration and from the mean of two or three trials calculate how much water must be added, and dilute until 1 cubic centimeter of this solution is exactly equivalent to 1 cubic centimeter of the silver solution. After this dilution, shake the solution well, to secure thorough mixing, and titrate another portion of the silver solution with it to make sure that it exactly matches the silver solution. This solution should be kept in a tightly stoppered bottle in a cool dark place. If protected from the air, it retains its exact strength for a long time.

DETERMINATIONS.

104. Determination of Chlorine.—Weigh from .2 to .3 gram of pure, dry sodium chloride into a beaker, and dissolve it in about 100 cubic centimeters of water. From a burette, introduce decinormal silver solution until all the chlorine is precipitated, and the solution contains a slight excess of silver. Note the exact amount of silver solution added. Now add 10 cubic centimeters of the ferric indicator, and determine the excess of silver in the solution by titration with sulphocyanide. The number of cubic centimeters of sulphocyanide used in titrating the excess of silver, subtracted from the total volume of silver nitrate added to the solution, gives the number of cubic centimeters of decinormal silver solution used in precipitating the chlorine; and this number multiplied by .003537 gives the weight of chlorine in the sample. Knowing this, and the weight of sample taken, the percentage of chlorine in the sample is readily calculated in the usual manner.

Sodium chloride is mentioned here because it is a handy salt to work with, and is easily obtained in a pure state. Of course, any other soluble chloride that admits of exact weighing would do just as well for practice, and ammonium chloride is frequently used.

Instead of weighing out .2 or .3 gram of sodium chloride, dissolving, and titrating directly, the following method is frequently employed: Weigh out 1 gram of sodium chloride, or a corresponding quantity of other chloride, dissolve it in water, dilute to 250 cubic centimeters in a graduated flask which holds exactly five times as much as a 50-cubic-centimeter pipette (see Art. **74**), and shake well to secure thorough mixing. By means of the pipette, which is known to be in harmony with the flask, remove 50 cubic centimeters of the solution to a beaker, dilute to 100 cubic centimeters, and run in a slight excess of decinormal silver solution. Now add 10 cubic centimeters of ferric indicator, and titrate the excess of silver with decinormal sulphocyanide. Repeat this titration with one or two more quantities of the original solution, and from the mean of the results yielded by these titrations calculate the percentage of chlorine in the sample. As the original sample is dissolved, and made up to 250 cubic centimeters, and 50 cubic centimeters of this solution are taken for titration, one-fifth of the weight of sample taken is used for each titration, and the calculation must be made accordingly. This, of course, may be done by multiplying the average of several titrations by 5, to obtain the volume of decinormal silver solution which would be required to precipitate the chlorine in the original sample, and using the weight of the original sample as a basis of calculation; or the average of several titrations may be taken as the volume of silver solution used, and one-fifth the weight of the original sample taken as the basis of calculation.

This method, if properly executed, probably yields more accurate results, as a rule, than those obtained by weighing out a small sample and titrating directly, for a slight error in weighing does not cause so serious an error in the results, as it is divided by 5, and by taking the average of two or more titrations a more accurate result is obtained than is possible with a single titration. This method of procedure may be applied in every case, and the results obtained by it are probably more trustworthy than those obtained by weighing up a small sample and titrating directly.

105. Determination of Bromine.—Weigh out .3 or .4 gram of potassium bromide, and dissolve it in from 100 to 200 cubic centimeters of water in a beaker. Add 10 cubic centimeters of the ferric indicator, and then from a burette run in a few drops of sulphocyanide to strongly color the solution, noting the exact volume of sulphocyanide added. Now, from another burette, run in decinormal silver solution, with constant stirring, until the color is completely removed from the solution. Then titrate back with decinormal sulphocyanide, until the last drop imparts a permanent color to the solution. The total amount of sulphocyanide added to the solution subtracted from the volume of silver solution used gives the quantity of silver solution used in precipitating the bromine, and this multiplied by .00798 gives the weight of bromine in the sample. In doing this, the sulphocyanide added to give the solution its color must be counted in.

Instead of weighing up a small sample and titrating directly, a sample weighing about 1 gram may be dissolved, and diluted to 250 cubic centimeters; and 50-cubic-centimeter quantities of this solution may be taken for titration, as in the determination of chlorine.

106. Determination of Iodine.—Dissolve about .3 gram of pure, dry potassium iodide in about 150 cubic centimeters of water in a glass-stoppered flask that will admit of vigorous shaking. From a burette run in the decinormal silver solution until there appears to be a slight excess; then add about .2 cubic centimeters more silver solution, stopper the flask, and shake vigorously to bring into reaction any soluble iodide that may be enclosed in the precipitate. Note the volume of silver solution used. Now add 10 cubic centimeters of the ferric indicator, and titrate with the decinormal sulphocyanide solution, giving the flask a rotary motion, as the sulphocyanide flows in, to mix the contents of the flask. When the solution assumes a red color, that appears to be permanent, place the stopper in the flask and shake vigorously, when, as a rule, the color will disappear. Continue

to add the sulphocyanide solution a drop at a time, shaking after each addition, until the solution assumes a red tinge, which is not destroyed by continued agitation. The volume of sulphocyanide used subtracted from the volume of silver solution added gives the amount of silver solution used in precipitating the iodine, and this number multiplied by .012685 gives the weight of iodine in the sample. From this the percentage is calculated in the usual manner.

107. Determination of Silver.—Weigh out accurately about .5 gram of pure, dry silver nitrate, and dissolve it in about 100 cubic centimeters of water in a beaker. Add 10 cubic centimeters of the ferric indicator, and titrate with decinormal sulphocyanide, stirring the solution as the sulphocyanide is added. As each drop of the sulphocyanide strikes the silver solution, it produces a reddish cloud, which immediately changes to a white precipitate upon stirring, and gives the solution a milky appearance. As the point of saturation is approached, the precipitate becomes flocculent and settles quickly; and finally a point is reached at which a drop of sulphocyanide produces a reddish tinge, which is not destroyed by stirring, showing that the reaction is complete. The number of cubic centimeters of sulphocyanide solution used multiplied by .010766 gives the weight of silver present, and from this the percentage is calculated.

It is just as well in making this determination to weigh out from 1 to 2 grams of silver nitrate, dissolve it in water, make the solution up to 250 cubic centimeters in a graduated flask, and withdraw several portions of 50 cubic centimeters each for titration. If this method is employed, each portion of 50 cubic centimeters should be diluted to about 100 cubic centimeters with water, and 10 cubic centimeters of ferric indicator added before titration.

108. Determination of Copper.—Weigh out 1 gram, or thereabouts, of pure, dry copper sulphate $CuSO_4,5H_2O$, and dissolve it in from 75 to 100 cubic centimeters of water in a graduated 250-cubic-centimeter flask. Heat this solution

to boiling, treat it with sulphurous acid until it smells distinctly of sulphur dioxide, and while hot, add an excess of decinormal sulphocyanide solution from a burette, noting the exact amount of sulphocyanide solution added. Allow the flask to stand until the solution cools to the temperature for which the flask is graduated. Then fill it exactly to the mark, mix thoroughly, and, using a dry funnel, filter through a dry filter paper into a perfectly dry, clean beaker.

By means of a pipette, remove 50 cubic centimeters of this filtrate to another beaker, dilute to 100 cubic centimeters with water, and add 10 cubic centimeters of indicator. Then from a burette, slowly add silver solution while constantly stirring the solution until the color is destroyed, and from another burette, cautiously introduce sulphocyanide, until the solution assumes a faint reddish tinge. This last quantity of sulphocyanide subtracted from the volume of silver solution used to decolorize the solution gives the amount of silver solution necessary to saturate the excess of sulphocyanide in 50 cubic centimeters of the original solution, and, as these solutions are matched, it, of course, represents the excess of sulphocyanide in 50 cubic centimeters of the solution.

Repeat this titration with a second and third portion of 50 cubic centimeters each, and take the average of the three titrations as representing the excess of sulphocyanide in 50 cubic centimeters of the solution. Multiplying this number by 5 gives the excess of sulphocyanide in the original solution, and subtracting this from the total amount of sulphocyanide added to the original solution gives the volume of sulphocyanide used to precipitate the copper. This number multiplied by .00632 gives the weight of copper in the sample, and from this the percentage of copper is readily calculated. The precipitate formed when sulphocyanide is added to a copper solution containing an excess of sulphurous acid is cuprous sulphocyanide $Cu_2(SCN)_2$. This method for copper is not accurate in the presence of chlorine, bromine, iodine, silver, mercury, or iron.

THE CYANIDE METHOD FOR COPPER.

109. Preparation of the Potassium-Cyanide Solution.—The potassium-cyanide solution used for this determination is usually made of such strength that each cubic centimeter of solution used represents .01 gram of copper. To make this solution, dissolve 28 grams of potassium cyanide in water, dilute to nearly 1 liter in a stoppered liter cylinder, and shake well to secure thorough mixing. Now weigh out exactly 1 gram of strictly pure copper foil, place it in a beaker of rather deep form, cover the beaker with a watch glass, and slowly add a little more dilute nitric acid than will be required to dissolve the copper, drawing the watch glass slightly to one side as the acid is added. Heat gently to aid the solution, and when all the copper is dissolved, evaporate the solution to a small bulk—say 12 or 15 cubic centimeters. Wash this solution into a graduated 250-cubic-centimeter flask, taking care that every particle of copper solution gets into this flask, dilute exactly to the mark, and mix the solution thoroughly.

By means of a pipette, remove 50 cubic centimeters of this solution to a beaker, dilute it to 200 cubic centimeters, add a strong solution of sodium carbonate, until a permanent precipitate is formed, and then add exactly 1 cubic centimeter of concentrate ammonia. This will generally dissolve the precipitate formed by the sodium carbonate, and leave a deep-blue solution, but whether the precipitate is all dissolved or not is immaterial. From a burette, slowly introduce the cyanide solution into this solution, while stirring it constantly, until the last drop removes the last trace of blue color.

As 1 gram of pure copper is dissolved, and one-fifth of the solution is taken for titration, the portion titrated contains .2 gram of metallic copper. Hence, in order to have 1 cubic centimeter of the potassium-cyanide solution represent .01 gram of copper, 20 cubic centimeters of this solution should be used to decolorize the copper solution. The potassium-cyanide solution, however, is purposely made stronger than

this, and from the quantity of it used to decolorize the copper solution, the amount that it must be diluted is calculated. The solution is now diluted almost to the calculated volume, mixed thoroughly, and two more quantities of 50 cubic centimeters each, are titrated in the same way that the first one was done. From the average of these two titrations, calculate how much water must be added to the solution, dilute accordingly, and mix the solution thoroughly. Then, as a check, titrate another quantity of 50 cubic centimeters of the original copper solution, diluting, neutralizing, and titrating in exactly the same way as the other portions. Exactly 20 cubic centimeters of the potassium cyanide should now be required to decolorize the copper solution.

Instead of dissolving exactly 1 gram of copper, making up the solution to 250 cubic centimeters, and using 50 cubic centimeters for titration, we may weigh out a smaller quantity of pure copper foil—say, approximately, .2 or .3 gram—place it in a beaker, dissolve in dilute nitric acid, evaporate the solution to about 3 cubic centimeters, dilute to 200 cubic centimeters with pure cold water, neutralize with sodium carbonate, add 1 cubic centimeter of concentrate ammonia, and titrate with the potassium-cyanide solution, as previously described. In this case the solution should be diluted nearly to the calculated volume, and mixed well. Then a second quantity of copper should be dissolved and the solution titrated after treating it in exactly the same way as the first one. From this result, calculate how much more the solution must be diluted, and add the calculated amount of water. The solution should now be tested before it is used, by dissolving and titrating another quantity of the copper.

In case pure copper foil is not at hand, pure crystallized copper sulphate $CuSO_4, 5H_2O$ may be used to standardize the cyanide solution. If this method is employed, weigh out about 1 gram of the pure salt, dissolve it in about 200 cubic centimeters of water and 1 cubic centimeter of nitric acid; neutralize with sodium carbonate, add 1 cubic centimeter of concentrate ammonia, and titrate with the potassium-cyanide solution. As the composition of copper sulphate is known,

the weight of copper in the solution thus made up is readily calculated, and from this the calculations are made, and the solution diluted in the same way that it is done when copper foil is used.

110. Determination of Copper.—Having now an accurately standardized solution of potassium cyanide, we are in a position to determine copper in its compounds or ores. The determination of copper in the sulphate serves well for practice. This is done as follows: Weigh out, accurately, 1 gram of pure copper-sulphate crystals $CuSO_4, 5H_2O$, and dissolve in a beaker, in 200 cubic centimeters of pure cold water, to which is added 1 cubic centimeter of nitric acid. To this solution, add a rather strong solution of sodium carbonate while stirring continuously, until the neutral point is reached and a permanent precipitate is formed. Then add 1 cubic centimeter of concentrate ammonia, which will generally dissolve the precipitate and leave a deep-blue solution. If this should fail, it makes no difference, as the cyanide will dissolve the precipitate, and there is enough ammonia present so that the point at which the reaction is complete may be easily recognized.

From a burette, slowly introduce the potassium-cyanide solution, while stirring the copper solution constantly, until the blue color is entirely destroyed. Note the volume of potassium-cyanide solution used to decolorize the copper solution, and from this, calculate the amount of copper. If exactly 1 gram of sample was taken for analysis, the percentage of copper may be read directly from the burette, as each cubic centimeter of solution used in this case represents 1 per cent. of copper. If any other weight of sample is taken, the weight of copper is obtained by multiplying the number of cubic centimeters of cyanide solution used by .01; and from this weight the percentage of copper in the sample is calculated in the usual manner.

It will probably be rather difficult at first to recognize the exact point at which this reaction is complete, but after a little practice the eye becomes accustomed to the change,

and the exact point is easily recognized. Great care must be taken to carry the titration to the same point in making actual determinations, as in standardizing the solution. In fact, all the conditions should be as nearly the same as possible. When this method was first used, sodium carbonate was not added, but the copper solution was simply rendered alkaline with an excess of ammonia, and titrated. It was soon found that the different quantities of ammonia added, and especially the varying proportions of copper and ammonia in different solutions, yielded discordant results. To overcome this difficulty, the solution is now usually neutralized with sodium carbonate, and only a small amount of ammonia is added. One cubic centimeter of concentrate ammonia is all that is really required, but if preferred, 2, 5, or even 10 cubic centimeters of ammonia may be used. When so much ammonia is added, however, great care must be taken to have as nearly as possible the same weight of copper in the solution when making a determination as when standardizing the solution, or the varying proportions of copper and ammonia will introduce an error in the work. It is necessary, of course, to add the same volume of ammonia in a determination that was added to the copper solution in standardizing, and it is desirable to have about the same amount of copper in the solution when making an actual determination that was used in standardizing the solution, even if the amount of ammonia added is small. Copper may be determined by this method in the presence of iron, but it is usually recommended to add some iron solution to the copper solution used in standardizing, when iron is to be present in the solution in which copper is determined.

NITRIC ACID.

111. Determination of Nitric Acid by Pelouze's Method.—Place a tubulated retort having a capacity of about 250 cubic centimeters on a water bath, with the neck of the retort slanting gently upwards, as shown in Fig. 16. Fit the

neck of this retort with a perforated rubber stopper, and through this perforation pass one end of a bent glass tube. Pass the other end of this tube through the perforation of a rubber stopper fitted into a **U** tube, thus connecting the retort and **U** tube. In this **U** tube place a little pure water, so that air or gas passing from the retort must bubble through it. Fit the tubulure of the retort with a perforated rubber stopper, and through this pass a glass tube extending a short

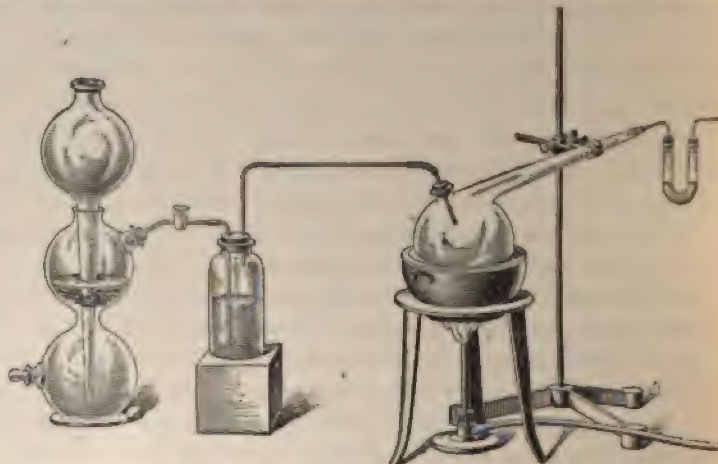

FIG. 16.

distance into the retort. Through this tube lead a current of carbon dioxide, which has been generated in a Kipp generator and washed in pure water, until the air is mostly, or entirely, expelled from the retort.

Disconnect the apparatus, and, with as little delay as possible, introduce into the retort from 30 to 40 cubic centimeters of pure concentrate hydrochloric acid, and about 1.5 grams of piano wire that has been accurately weighed. Then quickly close connections, and heat the retort on a water bath, while leading through it a gentle current of carbon dioxide, until the wire is completely dissolved. In an atmosphere of carbon dioxide, the iron all dissolves in hydrochloric acid to ferrous chloride $FeCl_2$.

While this action is going on, weigh accurately from .3 to .5 gram of pure potassium nitrate into a tube similar to the one employed to contain the sample in the determination of ammonium (see Art. **90**). When the wire is completely dissolved, increase the flow of carbon dioxide, remove the stopper from the mouth of the retort, introduce the tube containing the sample of potassium nitrate, and allow it to slide down the inclined neck of the retort into the liquid. Connect the apparatus again as quickly as possible, decrease the flow of carbon dioxide so that it passes through the **U** tube at the rate of about 2 bubbles per second, and continue to heat on the water bath for 15 or 20 minutes.

The reaction that takes place when the nitrate is introduced into the ferrous solution is

$$\begin{aligned} &3FeCl_2 + KNO_3 + 4HCl \\ &= 3FeCl_3 + KCl + NO + 2H_2O \end{aligned}$$

It will be complete at the end of 15 or 20 minutes, and the solution will usually have a dark color, due to the NO that is dissolved in it. Now remove the water bath, wipe the retort with a cloth until the outside of it is perfectly dry, and heat to boiling over the Bunsen burner. Continue the boiling a few minutes after the dark color has been removed, and the liquid has assumed the clear yellow color of ferric chloride, shaking the apparatus from time to time to prevent the deposition of dry salt on the sides of the retort. Remove the burner and regulate the flow of carbon dioxide so as to prevent any air from being drawn in through the **U** tube during the cooling and consequent contraction of the gases and vapors in the retort.

Allow the solution to cool to the temperature of the room while leading a gentle current of carbon dioxide through the retort. Then disconnect the apparatus, transfer the solution to a beaker, rinse out the retort thoroughly with cold water; adding the washings to the solution in the beaker, dilute this to about 300 cubic centimeters with pure cold water, and titrate at once with potassium bichromate, as described in Arts. **97** and **98**. This titration gives the amount of iron

v nains in the ferrous state, and this quantity subtracted from the total weight of iron taken gives the amount f iron oxidized by the nitrate. In making this calculation, it must be remembered that piano wire is not pure iron. In ordinary work it is sufficiently accurate to assume that the piano wire contains 99.6 per cent. of iron, but if great accuracy is required it is necessary to determine the exact percentage of iron in the wire by the gravimetric method described in Art. **14.**

From the above eq ll be seen that 28 parts of iron, oxidized from the fer. the ferric condition by the nitrate, correspond to 9 N_2O_5; hence the weight of N_2O_5 may be calculated by of a proportion as follows:

$$28 : 9 = \text{w} \quad \text{on oxidized} : x.$$

Then, having the weig ample taken, the percentage is readily calculated from this weight in the usual manner. The percentage of cid is always calculated as N_2O_5, but from this the pe ge of HNO_3 may be calculated if desired.

ATOMIC WEIGHTS USED.

112. It will be noticed that the atomic weights used in this paper are not, as a rule, those given in *Theoretical Chemistry*. The reason for this is that while the weights there given are taken from the most reliable sources, and are the results obtained by the latest determinations, they are not known to be, and probably are not, absolutely correct, as sufficient work has not been done on this subject to determine the exact weights with certainty. For this reason, it was thought best to use the weights most frequently employed in analytical chemistry, but if the student wishes to do so, he can easily substitute the weights given in *Theoretical Chemistry* in his calculations and in making up standard solutions.

It will also be noticed that in the case of compounds, the composition of which is not known for certain, the simplest

formula proposed has been used. Thus, potassium permanganate is written $KMnO_4$, rather than $K_2Mn_2O_8$, because it has not been determined with certainty which is correct, and $KMnO_4$ is the simplest. Of course, it makes no difference in the calculations whether 1 molecule of $K_2Mn_2O_8$ or 2 molecules of $KMnO_4$ enter into the reactions.

QUANTITATIVE ANALYSIS.

(PART 2.)

INTRODUCTION.

DESCRIPTIONS.

1. Remarks.—Having become familiar with the methods quantitative analysis, by making a number of determina-ons, the student is now in a position to proceed with the mplete analysis of chemical compounds, alloys, and min-ıls. But, before starting on this work, it is well to scribe a number of devices that, in many cases, shorten d simplify the operations. It was deemed best to defer se descriptions until this time, for the student should rn to work without making use of these methods, and ould become familiar with the properties of precipitates fore they are employed. In fact, these methods are dom, if ever, necessary, but are very handy in some cases.

FILTERING.

2. As we have seen, when a tube is attached to the lower d of a funnel, the increased weight of water tends to draw e liquid through the filter much more rapidly than it

would pass through without this weight drawing it. On the same principle, if rather strong suction is applied at the lower end of the funnel, and the filter paper is pressed so close to the sides of the funnel that no air can pass between the glass and paper, filtration, which is a tedious operation at best, will be materially shortened. This may be accomplished by placing the end of the funnel in a tight vessel from which the air is partially exhausted.

3. A Simple Filter Pump.—A simple form of filter pump is shown in Fig. 1. The flask *a* is made of strong

FIG. 1.

heavy glass to withstand pressure. It is fitted with a doubly perforated rubber stopper, through one perforation of which the tube of the funnel *b* is passed, while a glass tube, bent

.t right angles, passes through the other perforation. This ube is connected, by means of a rubber tube, with a glass ube passing through the stopper of the bottle *c*, which has . tubulure near the bottom. This tubulure is fitted with a ıerforated rubber stopper through which a glass tube is ıassed, and this glass tube is connected with a similar glass ube passing through the tubulure of the bottle *d* by means f a piece of rubber tubing.

The bottle *c* is now filled with water, the apparatus con- .ected, and *d* placed upon the floor. The water begins to ıass from *c* to *d*, leaving a partial vacuum in *c*, and some of he air passes over from the flask *a* to help fill this. A par- ial vacuum is thus produced in the flask *a*, and the liquid is lrawn through the filter to fill this. When all the water has ıassed from *c* to *d*, the bottle *d* may be placed upon the able, connected with the flask *a*, and *c* may be placed on the loor, thus causing the water to flow back; this may be epeated as often as necessary. It is very handy to have a crew pinch cock *e* on the tube connecting the two bottles, o prevent the flow of water from one to the other while heir positions are being changed.

This form of filter pump does not produce very strong uction, and, consequently, filtration is not nearly so rapid as vhen a stronger form of pump is used; but it is very handy n many cases, as it can be arranged in any laboratory in a 'ew minutes. If bottles having tubulures near the bottom ıre not at hand, ordinary large bottles may be used. In this :ase, the bottles are fitted with stoppers having two perfora- :ions, and are connected by a piece of rubber tubing attached :o glass tubes passing through the stoppers and nearly to the ɔottom of each bottle. The water is thus siphoned from one ɔottle to the other, and this works nearly as well as the form ;hown in the figure.

4. A Stronger Pump.—If the laboratory is supplied with running water, as every laboratory should be, a much more efficient pump, depending upon running water for the exhaustion of air, may be used. Aspirators depending upon

running water are made in several forms and of different materials. Both glass and metal aspirators may be purchased from dealers. A very good form of filter pump is shown in Fig. 2. The aspirator is connected with the faucet by means of a piece of strong rubber tubing, or a rubber band *d*, and is firmly bound to the faucet by means of a cord or wire.

FIG. 2.

The water flowing through the tube *b*, and out of the zigzag tube at the bottom, draws the air out of the bulb *a*, having a side tube *c* that is connected with the flask *e*, by means of a rubber tube having thick walls to withstand the pressure. With a strong water pressure, more than nine-tenths of the air may be exhausted from the flask *e* by means of this pump, thus producing strong suction, and, consequently, rapid filtration.

5. A Platinum Cone.—If we were to place a filter paper in a funnel in the ordinary manner, and apply suction,

by means of the pump just described, while filtering, the paper would immediately be broken. To avoid this breaking of the paper and consequent loss of precipitate, a platinum cone is always used to protect the cone of the filter. A platinum cone is shown at (*a*), Fig. 3, and at (*b*) it is shown placed in the funnel ready for use. It is merely a cone made of thin platinum, and filled with small perforations through which the liquid can pass, but which are too small to allow the suction to break the paper. The cone must fit the funnel perfectly, and the paper is then fitted into the funnel in the same way that would be done if the cone were not employed. Any amount of suction may now be applied without breaking the paper.

FIG. 3.

While this method of rapid filtration is very handy in many instances, it is not best to apply it in all cases. Precipitates that tend to run through the filter—notably zinc sulphide and barium sulphate—are much more likely to pass through when suction is applied than when allowed to filter in the usual manner. When several elements are to be successively separated from the same solution, there is increased danger of loss of solution if suction is applied in filtering; hence, if this method is employed in these cases, greater care should be taken to avoid such loss.

6. The Gooch Crucible.—A rapid method of filtering without paper is afforded by the Gooch crucible, which serves both as filter and crucible. It is similar to an ordinary platinum crucible, except that the bottom is filled with small perforations, and it is supplied with a platinum cap that fits

over the bottom. In Fig. 4 the crucible and cap are shown at (*a*), and the crucible fitted into the funnel tube as it is used in filtering is shown at (*b*). To use this crucible, fit it into the top of a funnel tube over which a short piece of thin flexible rubber tubing is stretched, as shown at (*b*). The rubber coming between the glass and crucible makes an air-tight connection. Insert the lower end of the funnel tube through a perforation of a rubber stopper into a filtering flask. Into the crucible pour a little prepared asbestos that has been scraped so that the fibers have a soft, silky texture, washed in acid to remove all impurities and suspended in pure water. Attach the flask to an aspirator, and draw the water through. The asbestos will be deposited on the bottom of the crucible in a firm, compact layer, which will retain the finest precipitates, and allow the liquid to pass through quite freely under the action of the filter pump. When all the water has passed through the crucible, wash the felt of asbestos two or three times with water, and suck the felt as dry as possible. Remove the crucible from the funnel tube; if any asbestos is on the outside of the crucible, wipe it off; place the cap on the bottom of the crucible, dry, ignite, cool, and weigh it. Replace the crucible in the funnel tube, apply suction, pour the liquid to be filtered through it in the same manner that it is poured through a filter, bring the precipitate on to the felt, and wash in the same way that is done when a filter paper is used. Remove the crucible from the tube, place the cap on the bottom, dry, ignite if necessary, and weigh.

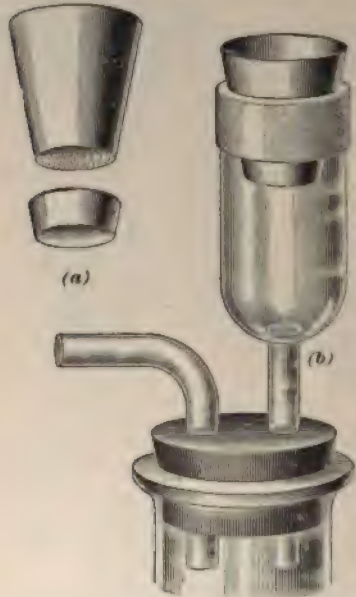

FIG. 4.

The increase in weight over the first weighing is the weight of precipitate.

This method of filtration and weighing is very handy in many cases. There is no paper present to reduce the precipitate during ignition, and all precipitates that do not attack platinum may be ignited in this crucible. Those precipitates that do attack platinum may be filtered in a porcelain crucible with a perforated bottom, similar in every way to the platinum crucible just described; hence, this method of filtration may be applied in every case. It is very often used in the case of precipitates that cannot be ignited. If a weighed filter is used in such cases, it is likely to change in weight, slightly, and thus render the results inaccurate; but, if the asbestos felt is properly made, the weight of a Gooch crucible scarcely varies at all, though it be washed, dried, and weighed, repeatedly.

IGNITING PRECIPITATES.

7. The ordinary method of igniting precipitates has already been described, and, generally speaking, this method is the best. But, in the case of precipitates that are not reduced when ignited in the presence of filter paper, much time is sometimes saved by igniting these precipitates without drying them. If this method of ignition is to be employed, draw the last of the wash water out of the precipitate, and filter as completely as possible by means of the filter pump. Fold the paper carefully around the precipitate in such a way that it will prevent particles from flying out and being lost, when heat is applied. Place the precipitate thus wrapped in the paper, in a crucible, place the cover on, stand it in a triangle, and heat gently over a Bunsen burner, turned very low, at first. Gradually increase the heat, by turning the flame higher, until the precipitate is perfectly dry, and the paper is charred. Then remove the burner for a moment, place the crucible in a slanting position, and partially withdraw the lid, as shown in Fig. 5. Replace the burner

under the crucible, and continue to heat it until the paper is completely burned off.

Placing the lid of the crucible in the position shown in the figure, hastens the burning of the filter, by causing a draft of air to pass through the crucible, thus supplying oxygen to burn the carbon. If the crucible and cover are placed in the proper position this current of air will not be strong enough to cause any loss of precipitate. This operation is rather slow in some cases, and is hastened by turning the crucible from time to time, so that each part of it is brought successively into the flame. If the paper is very slow in burning, it may sometimes be hastened by stirring the precipitate with a stout piece of platinum wire. When this is done, the burner must be removed while stirring, and great care must be taken to guard against loss. If the precipitate is one that requires intense ignition, a blast lamp may be substituted for the Bunsen burner, after the paper is charred; but in this case it is best to stand the crucible in an upright position, or at least take care that the flame strikes the crucible in such a way that it does not produce a strong draft of air through the top of it, for with a blast lamp it is easy to produce a current of air that will carry out particles of precipitate.

FIG. 5.

This method of ignition is very handy in many instances. The time that it saves in determining silica, iron, alumina, calcium, etc., the precipitates of which are not reduced by heating with carbon, is considerable. The danger of loss, however, is greater when this method is employed, and, consequently, greater care should be exercised.

THE ANALYSIS OF CHEMICAL COMPOUNDS.

COMPLETE ANALYSES.

8. In describing the analysis of compounds, it will not be necessary to give such full directions for the determination of the elements with which we have become familiar in *Quantitative Analysis*, Part 1, for the student should now be able to determine any of these elements without trouble; and if he is not, he can refer to *Quantitative Analysis*, Part 1, at any time. While the elements that have not been determined will need to be treated a little more fully than those that have, it will hardly be necessary to treat them so fully as were the determinations in *Quantitative Analysis*, Part 1, for, having become familiar with the general methods of quantitative analysis, the student should be able to apply them even in cases for which he has not had full directions.

In the analysis of chemical compounds the student has an additional check on his work, for, in addition to calculating the theoretical percentage of each element, or group of elements, determined, he can see how near the percentages obtained come to footing up to 100. For reasons that have already been explained, the sum of the percentages will rarely, if ever, be exactly 100; but, if the analyses are carefully performed, when working on simple compounds, the results obtained will frequently foot up to very near 100.

MAGNESIUM SULPHATE.

9. Preparation of the Sample.—The sample must be dry, but must not have lost water of crystallization. As this salt is slightly efflorescent, select 8 or 10 grams of crystals that are dry, but have not lost water of crystallization; pulverize them quickly by means of a mortar and pestle, and

it, wash the precipitate on the felt with hot water, and suck it as dry as possible by means of the filter pump. Place the cover on the crucible, and heat gently over the Bunsen burner to dry it; then ignite at a moderate heat, cool in a desiccator, and weigh as barium sulphate $BaSO_4$, which contains 34.33 per cent. of SO_3.

If a Gooch crucible is not at hand, the precipitate may be filtered on filter paper and treated as described in Arts. **66** and **67**, *Quantitative Analysis*, Part 1, which should be read in connection with this determination, but a filter pump should not be used, as this increases the danger of precipitate passing through the filter. Some chemists recommend the use of double filters for this precipitate. If this method is used, two filters are placed together, folded, and fitted into the funnel just like a single filter. This device seems to be more efficient than a single filter, in some cases.

12. Determination of Water.—For the determination of water, weigh a crucible, introduce about 1 gram of the sample, and weigh again. The difference in the two weights is the weight of sample taken. Place the crucible and contents over a Bunsen burner, and heat very gently at first, but gradually raise the temperature to dull redness. Heat at this temperature for 5 minutes, cool in a desiccator, and weigh. Then, again heat over the Bunsen burner, cool in a desiccator, and weigh; and repeat this operation till a constant weight is obtained. The loss in weight is the weight of water which has been expelled by the heat, and from this the percentage of water in the sample is readily calculated in the usual manner. In making this determination, sufficient heat must be employed to expel all the water, but a very high temperature is likely to decompose the salt, and, consequently, is to be avoided.

The theoretical composition of $MgSO_4, 7H_2O$ is as follows:

MgO	16.26%
SO_3	32.52%
H_2O	51.22%
	100.00%

cautiously over the Bunsen burner at a low temperature, with the crucible covered, and then raise the temperature to bright redness for several minutes. Cool in a desiccator and weigh as magnesium pyrophosphate $Mg_2P_2O_7$, which contains 36.04 per cent. of magnesia MgO. In connection with this determination, the student should read Arts. **34** and **35**, *Quantitative Analysis*, Part 1.

11. Determination of Sulphuric Acid.—Weigh about 1 gram of the sample into a beaker, dissolve it in 100 cubic centimeters of water, acidulate the solution with a few drops of hydrochloric acid, add from 5 to 10 cubic centimeters of ammonium chloride, heat to boiling, and precipitate the sulphuric acid with a slight excess of barium chloride. Continue the boiling a few moments while stirring the solution continuously, and then stand aside in a warm place for 2 or 3 hours for the precipitate to collect and settle.

As this finely divided precipitate tends to pass through filter paper, and is very easily reduced when ignited in the presence of carbonaceous matter, it is best to use a Gooch crucible in filtering it. If the Gooch felt is carefully prepared, it will easily retain every particle of precipitate. For this purpose, pour the asbestos into the crucible in the usual manner, and draw the water through. Then stand the bottle, in which the asbestos is suspended, aside, for a few moments, when the coarser and heavier part of the asbestos will sink to the bottom, and only the finest particles remain suspended in the water. Pour some of this into the crucible and draw the water through. The fine particles of asbestos will thus be deposited upon the coarser layer, forming a compact felt, which will retain the finest precipitates. This is not necessary with ordinary precipitates, and with such a felt, filtration is much slower than with a coarser one, but for very fine precipitates, the felt should always be prepared in this manner.

Draw as much water as possible out of the felt by means of the filter pump, then dry it carefully over a Bunsen burner, ignite moderately, cool in a desiccator, and weigh. Return the crucible to the funnel tube, decant the clear liquid through

it, wash the precipitate on the felt with hot water, and suck it as dry as possible by means of the filter pump. Place the cover on the crucible, and heat gently over the Bunsen burner to dry it; then ignite at a moderate heat, cool in a desiccator, and weigh as barium sulphate $BaSO_4$, which contains 34.33 per cent. of SO_3.

If a Gooch crucible is not at hand, the precipitate may be filtered on filter paper and treated as described in Arts. **66** and **67**, *Quantitative Analysis*, Part 1, which should be read in connection with this determination, but a filter pump should not be used, as this increases the danger of precipitate passing through the filter. Some chemists recommend the use of double filters for this precipitate. If this method is used, two filters are placed together, folded, and fitted into the funnel just like a single filter. This device seems to be more efficient than a single filter, in some cases.

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The theoretical composition of $MgSO_4, 7H_2O$ is as follows:

MgO	16.26%
SO_3	32.52%
H_2O	51.22%
	100.00%

BARIUM CHLORIDE.

13. If the sample is dry, pure, and in small crystals, no further preparation is required, but if it is in large crystals, it should be pulverized by means of a mortar and pestle, and preserved as described in Art. **9.**

This salt may be analyzed in several ways. The method most generally adopted, however, is as follows:

14. Determination of Barium.—Dissolve about 1 gram of the sample in 100 cubic centimeters of water, add 1 cubic centimeter of dilute hydrochloric acid and 5 cubic centimeters of ammonium chloride; heat the solution to boiling, and precipitate the barium, as barium sulphate, with a slight excess of dilute sulphuric acid. Continue the boiling for a few minutes, and then stand beaker and contents in a rather warm place for the precipitate to collect and settle.

It is a good plan to test the solution before filtering, to learn if sufficient acid has been added. To do this, remove a few drops of the clear supernatant liquid to a watch glass, and add a few drops of barium-chloride solution. If this produces a precipitate on the watch glass, it shows that the solution contains free sulphuric acid, and, consequently, that enough has been added to precipitate all the barium. If a precipitate is not formed, more dilute sulphuric acid must be added, and the solution must again be boiled and the precipitate allowed to settle. In either case, the portion taken out on the watch glass to be tested must be thrown away. When the precipitate has completely settled, filter, wash, ignite, and weigh, by one of the methods described in Art. **11.** The precipitate is barium sulphate, which contains 58.81 per cent. of barium, and from this the percentage of barium is readily calculated. In connection with this determination, Arts. **42** and **43,** *Quantitative Analysis*, Part 1, should be read.

15. Determination of Chlorine.—Dissolve .5 gram, or a trifle more, of the sample, in about 100 cubic centimeters

it, wash the precipitate on the felt with hot water, and suck it as dry as possible by means of the filter pump. Place the cover on the crucible, and heat gently over the Bunsen burner to dry it; then ignite at a moderate heat, cool in a desiccator, and weigh as barium sulphate $BaSO_4$, which contains 34.33 per cent. of SO_3.

If a Gooch crucible is not at hand, the precipitate may be filtered on filter paper and treated as described in Arts. **66** and **67**, *Quantitative Analysis*, Part 1, which should be read in connection with this determination, but a filter pump should not be used, as this increases the danger of precipitate passing through the filter. Some chemists recommend the use of double filters for this precipitate. If this method is used, two filters are placed together, folded, and fitted into the funnel just like a single filter. This device seems to be more efficient than a single filter, in some cases.

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13. If the sample is dry, pure, and in small crystals, no further preparation is required, but if it is in large crystals, it should be pulverized by means of a mortar and pestle, and preserved as described in Art. **9.**

This salt may be analyzed in several ways. The method most generally adopted, however, is as follows:

14. Determination of Barium.—Dissolve about 1 gram of the sample in 100 cubic centimeters of water, add 1 cubic centimeter of dilute hydrochloric acid and 5 cubic centimeters of ammonium chloride; heat the solution to boiling, and precipitate the barium, as barium sulphate, with a slight excess of dilute sulphuric acid. Continue the boiling for a few minutes, and then stand beaker and contents in a rather warm place for the precipitate to collect and settle.

It is a good plan to test the solution before filtering, to learn if sufficient acid has been added. To do this, remove a few drops of the clear supernatant liquid to a watch glass, and add a few drops of barium-chloride solution. If this produces a precipitate on the watch glass, it shows that the solution contains free sulphuric acid, and, consequently, that enough has been added to precipitate all the barium. If a precipitate is not formed, more dilute sulphuric acid must be added, and the solution must again be boiled and the precipitate allowed to settle. In either case, the portion taken out on the watch glass to be tested must be thrown away. When the precipitate has completely settled, filter, wash, ignite, and weigh, by one of the methods described in Art. **11.** The precipitate is barium sulphate, which contains 58.81 per cent. of barium, and from this the percentage of barium is readily calculated. In connection with this determination, Arts. **42** and **43,** *Quantitative Analysis*, Part 1, should be read.

15. Determination of Chlorine.—Dissolve .5 gram, or a trifle more, of the sample, in about 100 cubic centimeters

of water, heat very gently, and precipitate the chlorine with a slight excess of silver nitrate to which a little nitric acid has been added. Then raise the temperature while stirring continuously, until the liquid begins to boil. Allow the precipitate to settle, filter, wash, ignite, and weigh, as directed in Art. **12**, *Quantitative Analysis*, Part 1. The precipitate is silver chloride $AgCl$, which contains 24.73 per cent. of chlorine. From this, calculate the percentage of chlorine in the sample.

16. Determination of Water.—Weigh about 1 gram of the sample in a weighed crucible. Place this over a Bunsen burner and heat very gradually, until the crucible assumes a dull-red color. Heat at this temperature for about 5 minutes, cool in a desiccator, and weigh quickly. Heat again for about 5 minutes, cool in a desiccator, and weigh; and repeat the heating and weighing until a constant weight is obtained. Heat enough must be applied to drive off all the water, but care must be taken not to heat too highly or some of the chlorine will also be expelled. The loss in weight is the weight of the water expelled by the heat, and from this, the percentage of water in the sample is calculated. The theoretical composition of $BaCl_2,2H_2O$ is as follows:

Ba	56.17%
Cl	29.05%
H_2O	14.78%
	100.00%

FERROUS SULPHATE.

17. Determination of Iron.—Weigh 1 gram of the sample into a beaker, dissolve it in 100 cubic centimeters of water, add about 1 cubic centimeter of hydrochloric acid, heat to boiling, and oxidize the iron with a little concentrate nitric acid. Precipitate the iron from this boiling solution by means of a slight excess of ammonia. As soon as the precipitate settles, filter on to a paper, using the filter pump.

Wash the precipitate thoroughly with hot water, and suck it as dry as possible with the pump. Wrap the filter paper around the precipitate, place it in a platinum crucible, and ignite, gently at first, but finally at full redness for 5 minutes. Cool, and weigh as Fe_2O_3, which contains 90 per cent. of FeO.

Instead of determining the ferrous oxide in this way, the method described in Arts. **14** and **15**, *Quantitative Analysis*, Part 1, may be employed. These articles should be read in connection with this determination at all events. Or, 1 gram of the sample may be dissolved in water containing 10 or 15 cubic centimeters of acid, and titrated as described in Art. **95** or Art. **98**, *Quantitative Analysis*, Part 1. From the iron obtained in this way, the amount of ferrous oxide is calculated by the proportion $Fe : FeO =$ wt. $Fe : x$, and from this the percentage of FeO in the sample is calculated in the usual manner.

18. Determination of Sulphuric Acid.—Dissolve about 1 gram of the sample in 100 to 150 cubic centimeters of water, add 1 cubic centimeter of concentrate hydrochloric acid, and from 5 to 10 cubic centimeters of ammonium chloride. Heat the solution to boiling, and precipitate the sulphuric acid with a slight excess of barium chloride. Stand in a warm place for the precipitate to collect and settle, and then filter, wash, ignite, and weigh, as directed in Art. **11**. The precipitate is $BaSO_4$, which contains 34.33 per cent. of SO_3, and from this the percentage of SO_3 in the sample is calculated in the usual manner.

19. Determination of Water.—The water of crystallization in ferrous sulphate cannot be determined by heating a sample of the salt in a crucible and calling the loss water, for while the water is being driven off, the iron is gradually changed from the ferrous to the ferric condition. Consequently, the water must be driven off, absorbed, and weighed directly. The most convenient way of doing this is by means of the apparatus shown in Fig. 6. Draw a piece

of hard glass tubing (combustion tubing) out to a small tube at one end, and bend this at right angles. Support the tube—which should be 10 or 12 inches long—by means of an iron clamp or other suitable support. Fit the end *a* with a perforated rubber stopper, through which the end of the drying tube *e*, which is filled with dry, fused calcium chloride, is passed. Over the small end of the tube at *b*, slip one end of a rubber tube, the other end of which is attached to an aspirator, and draw a gentle current of air through the tube, while heating it throughout its entire

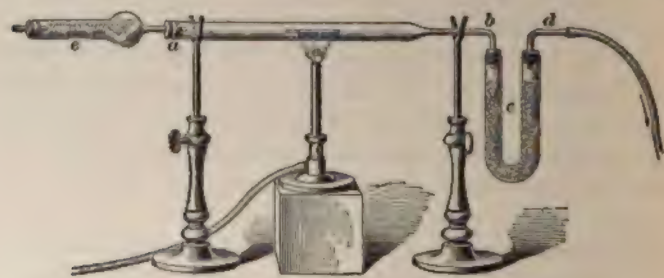

FIG. 6.

length by means of a Bunsen burner, to get it perfectly dry. Remove the rubber tube from *b*, and pass this end of the tube through the perforation in the stopper of one limb of a **U** tube *c*, that contains dry, fused calcium chloride, and has just been accurately weighed. Through the perforation in the stopper in the other limb of the tube, pass a small glass tube *d*, bent at right angles. Then withdraw the drying tube and stopper from *a*, introduce a boat made of platinum foil, containing about 1 gram of the sample that has been accurately weighed, and immediately replace the stopper and drying tube. Over the tube *d*, slip the end of a rubber tube that is connected with an aspirator, and draw a gentle current of air through the apparatus. Then bring a burner under the platinum boat containing the sample, and heat it at a gradually increasing temperature, until the water is all driven off. The current of air passing through the apparatus

will carry the aqueous vapors over to the **U** tube *c*, where they are absorbed by the calcium chloride. If any water condenses near the end of the tube at *b*, the tube must be heated at this point until this water is driven over and absorbed in the **U** tube. It is a good plan, at the end of the operation, to heat the tube *a b*, throughout its entire length, in order to be sure that all moisture is driven over and absorbed; and the current of air should be continued a few moments to draw all the moist air out of the tube *a b*. Then remove the **U** tube to the balance, and weigh as soon as it is cool.

Air should be excluded from the tube while it is cooling, or the calcium chloride is likely to absorb moisture from the air and thus increase in weight. This may be accomplished by placing a piece of glass rod in the perforation of the stopper through which the tube *b* passed, and drawing a short piece of rubber tubing over the tube *d*, and placing a glass rod in the other end of this rubber tube. Or, if the first weighing were performed without the tube *d*, this may be removed, and the perforation in this stopper may also be closed by means of a glass rod. These rods must be removed before weighing, unless they were in the perforations during the first weighing, as the conditions must be as nearly the same as possible during these two weighings; and if they are used during both weighings, one of them should be removed for a moment just before weighing, to allow any inequality of pressure to adjust itself. The increase in weight is the weight of water expelled from the sample, and absorbed by the calcium chloride, and from this the percentage of water in the sample is calculated in the usual manner.

Instead of weighing up a sample for each determination, the iron and sulphuric acid may be determined in the same sample, and this is sometimes an advantage on account of a small sample, or for some other reason. The method of analysis just described, is advised whenever practicable, but it is well to make one analysis as follows. Determine the iron just as described in Art. **17**, except that it is best to

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through the tube, while heating it throughout i

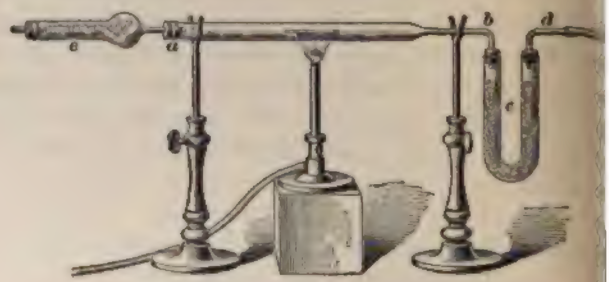

FIG. 6.

length by means of a Bunsen burner, to get it perfe
Remove the rubber tube from *b*, and pass this en
tube through the perforation in the stopper of one
a **U** tube *c*, that contains dry, fused calcium chloride,
just been accurately weighed. Through the perfo
the stopper in the other limb of the tube, pass a sm
tube *d*, bent at right angles. Then withdraw the
tube and stopper from *a*, introduce a boat made of
foil, containing about 1 gram of the sample that
accurately weighed, and immediately replace the sto
drying tube. Over the tube *d*, slip the end of a rub
that is connected with an aspirator, and draw a ge
rent of air through the apparatus. Then bring
under the platinum boat containing the sample, an
at a gradually increasing temperature, until the wa
driven off. The current of air passing through the a

of hard glass tubing (combustion tubing) out to a small tube at one end, and bend this at right angles. Support the tube—which should be 10 or 12 inches long—by means of an iron clamp or other suitable support. Fit the end *a* with a perforated rubber stopper, through which the end of the drying tube *e*, which is filled with dry, fused calcium chloride, is passed. Over the small end of the tube at *b*, slip one end of a rubber tube, the other end of which is attached to an aspirator, and draw a gentle current of air through the tube, while heating it throughout its entire

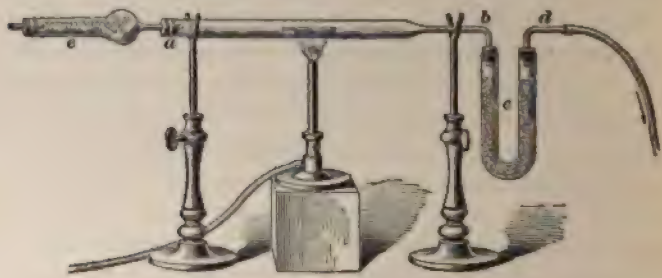

FIG. 6.

length by means of a Bunsen burner, to get it perfectly dry. Remove the rubber tube from *b*, and pass this end of the tube through the perforation in the stopper of one limb of a **U** tube *c*, that contains dry, fused calcium chloride, and has just been accurately weighed. Through the perforation in the stopper in the other limb of the tube, pass a small glass tube *d*, bent at right angles. Then withdraw the drying tube and stopper from *a*, introduce a boat made of platinum foil, containing about 1 gram of the sample that has been accurately weighed, and immediately replace the stopper and drying tube. Over the tube *d*, slip the end of a rubber tube that is connected with an aspirator, and draw a gentle current of air through the apparatus. Then bring a burner under the platinum boat containing the sample, and heat it at a gradually increasing temperature, until the water is all driven off. The current of air passing through the apparatus

will carry the aqueous vapors over to the **U** tube *c*, where they are absorbed by the calcium chloride. If any water condenses near the end of the tube at *b*, the tube must be heated at this point until this water is driven over and absorbed in the **U** tube. It is a good plan, at the end of the operation, to heat the tube *a b*, throughout its entire length, in order to be sure that all moisture is driven over and absorbed; and the current of air should be continued a few moments to draw all the moist air out of the tube *a b*. Then remove the **U** tube to the balance, and weigh as soon as it is cool.

Air should be excluded from the tube while it is cooling, or the calcium chloride is likely to absorb moisture from the air and thus increase in weight. This may be accomplished by placing a piece of glass rod in the perforation of the stopper through which the tube *b* passed, and drawing a short piece of rubber tubing over the tube *d*, and placing a glass rod in the other end of this rubber tube. Or, if the first weighing were performed without the tube *d*, this may be removed, and the perforation in this stopper may also be closed by means of a glass rod. These rods must be removed before weighing, unless they were in the perforations during the first weighing, as the conditions must be as nearly the same as possible during these two weighings; and if they are used during both weighings, one of them should be removed for a moment just before weighing, to allow any inequality of pressure to adjust itself. The increase in weight is the weight of water expelled from the sample, and absorbed by the calcium chloride, and from this the percentage of water in the sample is calculated in the usual manner.

Instead of weighing up a sample for each determination, the iron and sulphuric acid may be determined in the same sample, and this is sometimes an advantage on account of a small sample, or for some other reason. The method of analysis just described, is advised whenever practicable, but it is well to make one analysis as follows. Determine the iron just as described in Art. **17**, except that it is best to

filter and wash the precipitate without the use of the filter pump, and great care must be taken not to lose any of the filtrate, or to allow any foreign matter to get into it. After the iron has been separated, render the filtrate slightly acid with hydrochloric acid, bring it to boiling, and precipitate the sulphuric acid with a slight excess of barium chloride. After allowing the precipitate to collect and settle while standing in a warm place, filter, wash, ignite, and weigh, as described in Art. **11.**

If, for any reason, it is necessary to do so, all three determinations may be made, using but one sample, but this usually involves considerable difficulty. If, however, this is to be done, weigh, accurately, about 1 gram of the sample into a platinum boat, and determine the water as just directed, taking care not to lose any of the sample out of the boat. At the completion of this determination, remove the platinum boat from the tube to a beaker, and dissolve the dry sample. This usually causes considerable trouble, and is generally best accomplished by heating for some time with concentrate hydrochloric acid, until most of the excess of acid is evaporated, and then diluting with water. When the sample is all dissolved off of the platinum boat, remove it from the solution, and wash it off thoroughly, receiving the washings in the main solution. Heat the solution to boiling, add a little concentrate nitric acid to oxidize any iron that may still be in the ferrous condition, and precipitate the iron with a slight excess of ammonia. Filter, wash with hot water, ignite, and weigh, as usual. Render the filtrate slightly acid with hydrochloric acid, heat to boiling, and precipitate the sulphuric acid with a slight excess of barium chloride. After standing in a warm place until the precipitate has collected and settled, filter, wash, ignite, and weigh, as directed in Art. **11.**

The theoretical composition of $FeSO_4,7H_2O$ is as follows:

FeO	25.90%
SO_3	28.78%
H_2O	45.32%
	100.00%

CALCIUM CARBONATE.

'0. Determination of Lime.—Heat the sample in an bath for 15 or 20 minutes at about 110°, to dry it; cool in siccator, and weigh out about .5 gram for the determina- of lime. Transfer this to a beaker of rather deep form, cover the beaker with a watch glass. Draw this slightly one side, introduce a few drops of hydrochloric acid, wing it to run down the side of the beaker, and quickly the watch glass back in place, to prevent any loss of stance during solution. Continue to add acid in this way il enough has been added to dissolve all the carbonate, complete the solution with the aid of heat, if necessary. ute the solution to about 100 cubic centimeters with pure er, render it strongly alkaline with ammonia, heat to ing, and precipitate the calcium with a moderate excess ammonium oxalate, adding the reagent slowly, and with stant stirring. Stand the beaker and contents in a warm ce for about 4 hours for the precipitate to collect and le. Filter, wash thoroughly with hot water, and deter- e the calcium oxide by one of the following methods:

. Dry the precipitate, remove it to a watch glass, burn filter in a platinum crucible, add the precipitate, ignite, l, and weigh, as directed in Art. **38**, *Quantitative Analy-* Part 1. The precipitate in this case is calcium oxide, the percentage is calculated by dividing the weight of the cipitate by the weight of sample taken, and multiplying result by 100, or, what amounts to the same thing, ving the decimal point two places to the right.

. Dry the precipitate, remove it as completely as possi- from the paper, and burn the filter in a porcelain crucible. d the precipitate, and moisten it with concentrate sul- ric acid. Heat gently to convert the precipitate into phate and drive off the excess of acid, ignite at a mod- te temperature over the Bunsen burner, cool, and weigh, as cium sulphate, following the directions given in Art. **40**, *antitative Analysis*, Part 1. The precipitate contains 18 per cent. of calcium oxide.

filter and wash the precipitate without the use of the pump, and great care must be taken not to lose any filtrate, or to allow any foreign matter to get into it. the iron has been separated, render the filtrate slightl with hydrochloric acid, bring it to boiling, and preci the sulphuric acid with a slight excess of barium chl After allowing the precipitate to collect and settle standing in a warm place, filter, wash, ignite, and wei described in Art. **11.**

If, for any reason, it is necessary to do so, all three minations may be made, using but one sample, bu usually involves considerable difficulty. If, however, to be done, weigh, accurately, about 1 gram of the sa into a platinum boat, and determine the water as directed, taking care not to lose any of the sample out boat. At the completion of this determination, remov platinum boat from the tube to a beaker, and dissolve th sample. This usually causes considerable trouble, a generally best accomplished by heating for some time concentrate hydrochloric acid, until most of the exce acid is evaporated, and then diluting with water. Whe sample is all dissolved off of the platinum boat, remo from the solution, and wash it off thoroughly, receivin washings in the main solution. Heat the solution to bo add a little concentrate nitric acid to oxidize any iron may still be in the ferrous condition, and precipitate the with a slight excess of ammonia. Filter, wash witl water, ignite, and weigh, as usual. Render the fil slightly acid with hydrochloric acid, heat to boiling, precipitate the sulphuric acid with a slight excess of ba chloride. After standing in a warm place until the pr tate has collected and settled, filter, wash, ignite, and w as directed in Art. **11.**

The theoretical composition of $FeSO_4,7H_2O$ is as foll

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SO_3	28.78%
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Dry the precipitate, remove it to a watch glass, burn r in a platinum crucible, add the precipitate, ignite, d weigh, as directed in Art. **38,** *Quantitative Analy-* t 1. The precipitate in this case is calcium oxide, percentage is calculated by dividing the weight of the te by the weight of sample taken, and multiplying lt by 100, or, what amounts to the same thing, the decimal point two places to the right.

ry the precipitate, remove it as completely as possi- the paper, and burn the filter in a porcelain crucible. precipitate, and moisten it with concentrate sul- acid. Heat gently to convert the precipitate into and drive off the excess of acid, ignite at a mod- mperature over the Bunsen burner, cool, and weigh, as sulphate, following the directions given in Art. **40,** *ative Analysis*, Part 1. The precipitate contains r cent. of calcium oxide.

filter and wash the precipitate without the use of the filter pump, and great care must be taken not to lose any of the filtrate, or to allow any foreign matter to get into it. After the iron has been separated, render the filtrate slightly acid with hydrochloric acid, bring it to boiling, and precipitate the sulphuric acid with a slight excess of barium chloride. After allowing the precipitate to collect and settle while standing in a warm place, filter, wash, ignite, and weigh, as described in Art. **11.**

If, for any reason, it is necessary to do so, all three determinations may be made, using but one sample, but this usually involves considerable difficulty. If, however, this is to be done, weigh, accurately, about 1 gram of the sample into a platinum boat, and determine the water as just directed, taking care not to lose any of the sample out of the boat. At the completion of this determination, remove the platinum boat from the tube to a beaker, and dissolve the dry sample. This usually causes considerable trouble, and is generally best accomplished by heating for some time with concentrate hydrochloric acid, until most of the excess of acid is evaporated, and then diluting with water. When the sample is all dissolved off of the platinum boat, remove it from the solution, and wash it off thoroughly, receiving the washings in the main solution. Heat the solution to boiling, add a little concentrate nitric acid to oxidize any iron that may still be in the ferrous condition, and precipitate the iron with a slight excess of ammonia. Filter, wash with hot water, ignite, and weigh, as usual. Render the filtrate slightly acid with hydrochloric acid, heat to boiling, and precipitate the sulphuric acid with a slight excess of barium chloride. After standing in a warm place until the precipitate has collected and settled, filter, wash, ignite, and weigh, as directed in Art. **11.**

The theoretical composition of $FeSO_4, 7H_2O$ is as follows:

FeO	25.90%
SO_3	28.78%
H_2O	45.32%
	100.00%

CALCIUM CARBONATE

20. Determination of Lime.—Heat the sample in an air bath for 15 or 20 minutes at about 110°, to dry it. Cool in a desiccator, and weigh out about .5 gram for the determination of lime. Transfer this to a beaker of rather large form and cover the beaker with a watch glass. Draw this slightly to one side, introduce a few drops of hydrochloric acid, allowing it to run down the side of the beaker, and quickly slip the watch glass back in place to prevent any loss of substance during solution. Continue to add acid in this way until enough has been added to dissolve all the carbonate and complete the solution with the aid of heat, if necessary. Dilute the solution to about 100 cubic centimeters with pure water, render it strongly alkaline with ammonia, heat to boiling, and precipitate the calcium with a moderate excess of ammonium oxalate, adding the reagent slowly and with constant stirring. Stand the beaker and contents in a warm place for about 4 hours for the precipitate to collect and settle. Filter, wash thoroughly with hot water, and determine the calcium oxide by one of the following methods:

1. Dry the precipitate, remove it to a watch glass, burn the filter in a platinum crucible, add the precipitate, ignite, cool, and weigh, as directed in Art. **38,** *Quantitative Analysis*, Part 1. The precipitate in this case is calcium oxide, and the percentage is calculated by dividing the weight of the precipitate by the weight of sample taken, and multiplying this result by 100, or, what amounts to the same thing, moving the decimal point two places to the right.

2. Dry the precipitate, remove it as completely as possible from the paper, and burn the filter in a porcelain crucible. Add the precipitate, and moisten it with concentrate sulphuric acid. Heat gently to convert the precipitate into sulphate and drive off the excess of acid, ignite at a moderate temperature over the Bunsen burner, cool, and weigh, as calcium sulphate, following the directions given in Art. **40,** *Quantitative Analysis*, Part 1. The precipitate contains 41.18 per cent. of calcium oxide.

filter and wash the precipitate without the use of the filter pump, and great care must be taken not to lose any of the filtrate, or to allow any foreign matter to get into it. After the iron has been separated, render the filtrate slightly acid with hydrochloric acid, bring it to boiling, and precipitate the sulphuric acid with a slight excess of barium chloride. After allowing the precipitate to collect and settle while standing in a warm place, filter, wash, ignite, and weigh, as described in Art. **11.**

If, for any reason, it is necessary to do so, all three determinations may be made, using but one sample, but this usually involves considerable difficulty. If, however, this is to be done, weigh, accurately, about 1 gram of the sample into a platinum boat, and determine the water as just directed, taking care not to lose any of the sample out of the boat. At the completion of this determination, remove the platinum boat from the tube to a beaker, and dissolve the dry sample. This usually causes considerable trouble, and is generally best accomplished by heating for some time with concentrate hydrochloric acid, until most of the excess of acid is evaporated, and then diluting with water. When the sample is all dissolved off of the platinum boat, remove it from the solution, and wash it off thoroughly, receiving the washings in the main solution. Heat the solution to boiling, add a little concentrate nitric acid to oxidize any iron that may still be in the ferrous condition, and precipitate the iron with a slight excess of ammonia. Filter, wash with hot water, ignite, and weigh, as usual. Render the filtrate slightly acid with hydrochloric acid, heat to boiling, and precipitate the sulphuric acid with a slight excess of barium chloride. After standing in a warm place until the precipitate has collected and settled, filter, wash, ignite, and weigh, as directed in Art. **11.**

The theoretical composition of $FeSO_4, 7H_2O$ is as follows:

FeO	25.90%
SO_3	28.78%
H_2O	45.32%
	100.00%

CALCIUM CARBONATE.

20. Determination of Lime.—Heat the sample in an air bath for 15 or 20 minutes at about 110°, to dry it; cool in a desiccator, and weigh out about .5 gram for the determination of lime. Transfer this to a beaker of rather deep form, and cover the beaker with a watch glass. Draw this slightly to one side, introduce a few drops of hydrochloric acid, allowing it to run down the side of the beaker, and quickly slip the watch glass back in place, to prevent any loss of substance during solution. Continue to add acid in this way until enough has been added to dissolve all the carbonate, and complete the solution with the aid of heat, if necessary. Dilute the solution to about 100 cubic centimeters with pure water, render it strongly alkaline with ammonia, heat to boiling, and precipitate the calcium with a moderate excess of ammonium oxalate, adding the reagent slowly, and with constant stirring. Stand the beaker and contents in a warm place for about 4 hours for the precipitate to collect and settle. Filter, wash thoroughly with hot water, and determine the calcium oxide by one of the following methods:

1. Dry the precipitate, remove it to a watch glass, burn the filter in a platinum crucible, add the precipitate, ignite, cool, and weigh, as directed in Art. **38,** *Quantitative Analysis*, Part 1. The precipitate in this case is calcium oxide, and the percentage is calculated by dividing the weight of the precipitate by the weight of sample taken, and multiplying this result by 100, or, what amounts to the same thing, moving the decimal point two places to the right.

2. Dry the precipitate, remove it as completely as possible from the paper, and burn the filter in a porcelain crucible. Add the precipitate, and moisten it with concentrate sulphuric acid. Heat gently to convert the precipitate into sulphate and drive off the excess of acid, ignite at a moderate temperature over the Bunsen burner, cool, and weigh, as calcium sulphate, following the directions given in Art. **40,** *Quantitative Analysis*, Part 1. The precipitate contains 41.18 per cent. of calcium oxide.

3. Wash the precipitate into a beaker as completely as possible with water, and then continue the washing with hot dilute sulphuric acid. Dissolve the precipitate in water and sulphuric acid. Heat the solution to 70° or 80°, and titrate with a potassium-permanganate solution, as directed in Art. **100**, *Quantitative Analysis*, Part 1. The strength of a permanganate solution with respect to CaO is there given.

21. Determination of Carbon Dioxide.—Carbon dioxide may be determined either by direct weighing, or by loss in weight. A number of methods of accomplishing this have been proposed. Three of those most commonly used are here given.

1. Fit a flask (b, Fig. 7), having a capacity of from 300 to 500 cubic centimeters, with a rubber stopper having three

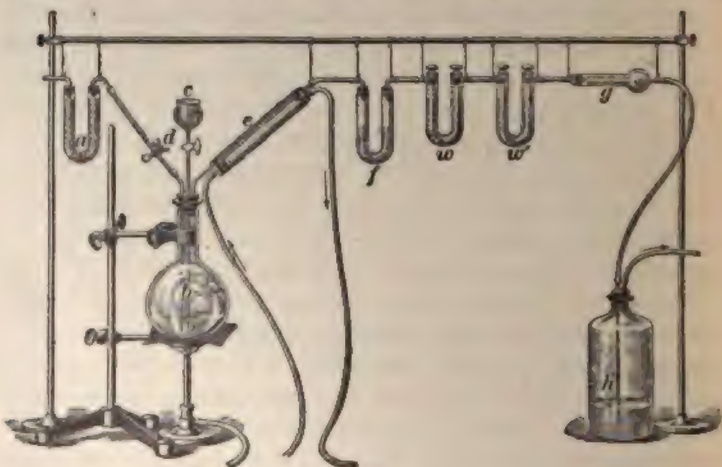


FIG. 7.

perforations. Through one of these perforations pass a funnel tube c, reaching nearly to the bottom of the flask. After passing this through the stopper, draw the lower end out to a rather small point, and bend it upwards to prevent the entrance of bubbles of gas. Through another opening, pass a tube, also reaching nearly to the bottom of the flask, and connect it with the U tube a, containing soda lime, or a

concentrate solution of sodium hydrate, by means of a rubber tube. Over this rubber tube, slip a pinch cock *d* that should be left open for the present, and is only to be used in case it becomes necessary later. Through the third perforation, pass a tube, reaching just through the stopper, into the neck of the flask. Bend this tube above the stopper, and pass it through the short cooler tube *e*.

A condenser for this purpose may be made by fitting each end of a short large tube with a doubly perforated rubber stopper, and passing the tube from the flask through one perforation of each of these stoppers. Through the other perforation of each stopper, pass short glass tubes, and connect these with rubber tubes. Through one of these tubes conduct cold water into the lower end of the condenser, and through the other conduct water from the upper end of the condenser to a sink. Connect the tube passing through this condenser with the U tube *f*, which is filled with pumice stone saturated with concentrate sulphuric acid, or is about half filled with glass beads, and contains enough concentrate sulphuric acid so that any air or gas passing through the tube must pass through the acid. Connect this U tube with the weighed U tube *w*, which is filled to three-fourths its capacity with soda lime, and the last quarter with rather fine, dry calcium chloride. Connect this with the weighed U tube *w'*, which is filled with soda lime and calcium chloride, in the same way that *w* is. For the U tubes *w* and *w'*, glass-stoppered weighing tubes are best used, but this is not necessary. Any tightly stoppered U tube that has been filled with soda lime and a little calcium chloride, and weighed, will answer the purpose. Connect the tube *w'* with the tube *g*, filled with dry, fused calcium chloride, to prevent the entrance of any moisture from this end. This tube may be connected directly with an aspirator, but, in order to better control the current of air and gas, it is best to connect it with the bottle *h*, containing concentrate sulphuric acid, so that the rate at which bubbles pass through this may be noted, and connect this bottle with an aspirator.

The flask *b* should be supported on a retort stand, and the

rest of the apparatus may be suspended by means of wire hooks, from a bar, or a thick piece of glass tubing, held in a clamp. A broom handle may be made to serve very well for this purpose. When all is in readiness, introduce enough pure water through the funnel tube *c*, to cover the end of this tube and the tube leading from *a*, draw a gentle current of air through the apparatus, and by means of a burner, heat the flask until the water commences to boil, while keeping air enough passing through the apparatus so that there is no back pressure towards *a*. Have an accurately weighed sample of calcium carbonate in a short open tube, ready. About .5 gram of sample is a good quantity, and the bottom of a test tube serves well to hold the sample. When the water commences to boil, withdraw the stopper from the flask, drop in the tube containing the sample, and return the stopper to its place at once. The water should be kept gently boiling, but the boiling should not be violent enough so that steam passes more than one-third of the way up the condenser, and it must not pass the middle of the condenser any way. Have the funnel tube *c* filled with half-strength hydrochloric acid, and by turning the stop-cock, allow a very little of this to flow into the flask. This will decompose the carbonate, setting free carbon dioxide, which passes over with the air and is absorbed by the soda lime. The acid should be added in very small amounts, or the evolution of carbon dioxide will be too rapid, and will cause a back pressure. The air should pass through the flask all the time, or at least there should be no back pressure towards *a*, and if such occurs, it should be checked at once, by closing the pinch cock *d* on the rubber tube, and leaving it closed until the evolution of gas slackens considerably.

When the evolution of carbon dioxide slackens, add a little more acid, and continue this treatment until the sample is completely decomposed, and the solution contains considerable free acid. Keep the solution gently boiling during this decomposition, but proceed slowly with this operation, and at no time allow condensation to be visible higher than the first third of the condenser. When solution is complete,

continue to draw air through the apparatus for 15 or 20 minutes, keeping the water in the flask as near the boiling point as possible. The carbon dioxide will all be carried over and absorbed in the weighing tubes by this time. Disconnect the apparatus, turn the stoppers of the weighing tubes so that air cannot pass through, remove them to the balance, and allow them to assume the temperature of the room. As soon as the tubes become cool, turn the stoppers for a moment to allow the air pressure to adjust itself, and then weigh the tubes. The increase in weight is the weight of carbon dioxide absorbed, and from this the percentage of carbon dioxide in the sample is readily calculated. There should be but a slight increase in the weight of *w′*.

If the operation is repeated, the tube *f*, containing sulphuric acid, must be emptied and refilled after each determination, but the weighing tubes may be used again in the same order. After two determinations, however, *w′* should be substituted for *w*, and *w* is refilled and used in the place of *w′*. In this way, the order in which the tubes are used is reversed, and one of the tubes is refilled after every second determination.

2. A simple form of apparatus for the determination of carbon dioxide by loss of weight, is shown in Fig. 8. It con-

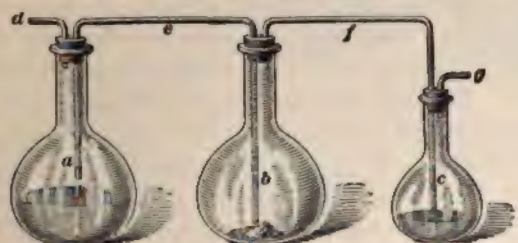


FIG. 8.

sists of three small flasks, two of which, *a* and *b*, should have a capacity of about 100 cubic centimeters each, and the third, *c*, should have a capacity of about 25 cubic centimeters. If, for any reason, it is desirable to use smaller flasks, 50 or 75 cubic-centimeter flasks may be used for *a* and *b*, but it

is generally best in this case to use a smaller sample, and greater care should be taken in performing the operation.

Fit each flask with a doubly perforated rubber stopper. Through the first perforation of the stopper in *a*, pass a small piece of glass tubing *d*, reaching just through the stopper, and bent at right angles above the stopper. About 2 inches is a good length for this tube. Through the second perforation of this stopper, pass one limb of the tube *e*, which is bent twice at right angles, so that it reaches nearly to the bottom of the flask, and pass the other limb through the first perforation of the stopper in *b*, and nearly to the bottom of the flask. Through the second perforation of the stopper in *b*, pass the short limb of the tube *f*, which is bent twice at right angles, so that the end just reaches through the stopper into the neck of the flask, and pass the long limb through the first perforation of the stopper in *c*, and nearly to the bottom of the flask. Through the other perforation of this stopper, pass a tube *g*, about 2 inches long, and bend it at right angles above the stopper.

Into the flask *a*, introduce about 40 cubic centimeters of half-strength nitric or hydrochloric acid; weigh accurately about 1 gram of the sample into *b*, and place about 10 cubic centimeters of concentrate sulphuric acid in *c*. Connect the apparatus, and weigh it carefully.

Place a piece of rubber tubing over the tube *g*, and by gently sucking on this, draw a very little of the acid from *a* over to *b*. Then immediately close the tube *d*, by slipping over it one end of a short rubber tube, the other end of which is closed by a piece of glass rod. The carbon dioxide that is evolved passes through the flask *c*, where any moisture that it carries with it is absorbed by the sulphuric acid. As soon as the effervescence in *b* ceases, remove the tube from *d*, draw a little more acid over from *a*, and immediately close *d* again. Repeat this operation until the carbonate is completely decomposed, and the flask *b* contains some free acid. Now place this flask over a Bunsen burner, and heat it gently until the solution just begins to boil. Remove the burner, withdraw the glass rod from the rubber tube

over *d*, and in its place insert a small drying tube filled with equal parts of dry calcium chloride and soda lime; connect *g* with an aspirator, and draw a little more than half a liter of air through the apparatus. This will suffice to remove all the carbon dioxide from the apparatus, and a larger quantity should be avoided. The air should not pass through the flasks faster than 2 or 3 bubbles per second. When all the carbon dioxide has been removed from the apparatus, allow it to stand till perfectly cool. Then remove the aspirator from *g*, and the drying tube from *d*, and weigh the apparatus at once. The difference in weight is the weight of carbon dioxide that has been expelled, and from this the percentage of carbon dioxide is readily calculated. It is the writer's experience, that the results obtained by this method are not as accurate as those obtained by the first method.

It may be mentioned at this point, that in determining the carbon dioxide united with metals whose sulphates are soluble, this method may be modified in a way that renders it more satisfactory. For this method, the apparatus shown in Fig. 9 is used. The two flasks, *a* and *b*, usually have a capacity of about 100 cubic centimeters each, though smaller flasks may be used, if desirable. Fit each of these flasks with a doubly perforated rubber stopper. Through the first perforation in the stopper of the flask *a*, pass a piece of glass tubing about 2 inches long, and bend it at right angles above the stopper. Through the other perforation of this stopper pass the long limb of the tube *e*, which is bent twice at right angles, so that it reaches nearly to the bottom of the flask. Pass the short limb of this tube through the first perforation in the stopper of *b*, and through the other perforation pass the tube *d*, reaching nearly to the bottom of the flask, and bent at right angles above the stopper.

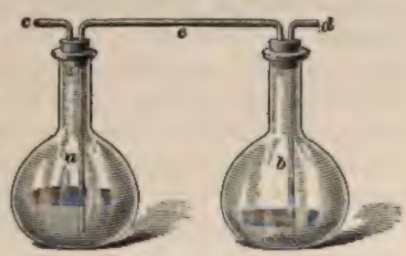


FIG. 9.

about 1 gram of the calcium carbonate and weigh again. The weight of the sample taken and the total weight of crucible, sample, and borax are thus obtained. The sample and borax should be present in about the proportion of 1 : 4 or 1 : 5. Place the crucible over a burner, heat gradually to redness, and maintain this temperature until the contents are in a state of quiet fusion, but avoid excessive heat. Some bubbles of carbon dioxide will remain in the fused mass, but these do not influence the result. Remove the burner, and when the contents of the crucible become solid, place it in a desiccator, allow it to cool, and weigh. The loss in weight is the weight of carbon dioxide, and from this the percentage of carbon dioxide is calculated.

This method yields accurate results if carefully performed. Borax may be fused at a red heat for half an hour without any appreciable loss of weight, but is volatilized quite rapidly at a white heat.

The theoretical composition of calcium carbonate is as follows:

CaO	56.00%
CO_2	44.00%
	100.00%

MANGANOUS CHLORIDE.

22. Determination of Manganese.—Manganese may be determined by several methods, only two of which, one gravimetric and one volumetric, will be given.

1. *Gravimetric Method.*—Dissolve 1 gram of the sample in about 100 cubic centimeters of water in a porcelain dish, heat the solution to boiling, and precipitate the manganese by slowly adding a slight excess of sodium carbonate, while stirring the solution continuously. Continue to boil the solution for a few minutes, and then stand the dish and contents in a warm place for the precipitate to collect and settle. If there is no hurry for the analysis, it is best to let it stand for 12 hours for the last particles of manganese to separate, but this is not necessary, for scarcely any ce

Fill the flask *a* to about half its capacity with concentrate sulphuric acid. Weigh about 1 gram of the sample into *b*, and then fill this flask to about one-third its capacity with pure water. Connect the apparatus and weigh it accurately. Close the tube *d* by drawing over it one end of a short rubber tube, the other end of which is closed by a piece of glass rod, and slip the end of a rubber tube over *c*. By sucking on this tube, draw enough air out of *b* so that when the mouth is removed from this tube a few drops of sulphuric acid will pass through the tube *e* from *a* to *b*. This decomposes the carbonate, and the liberated carbon dioxide passes through *e*, is dried by the sulphuric acid in *a*, and escapes through *c*. When effervescence ceases, draw some more air out, thus causing a few more drops of acid to pass over to *b*, and repeat this till the carbonate is entirely decomposed. Then suck quite vigorously on the tube attached to *c*, to cause considerable acid to flow over to *b*, thus heating the solution sufficiently to expel any carbon dioxide that it may contain. Now remove the rod from the end of the rubber tube slipped over *d*, attach a drying tube containing calcium chloride and soda lime in its place, connect *c* with an aspirator, and draw about half a liter of air through the apparatus at the rate of 2 bubbles per second. This will remove all the carbon dioxide from the apparatus, and as it passes through the sulphuric acid, any moisture carried over with the gas is absorbed. Allow the apparatus to stand till it is perfectly cool, then remove the tubes from *c* and *d*, and weigh the apparatus at once. The loss in weight is the weight of carbon dioxide expelled, and from this the percentage of carbon dioxide is calculated.

3. A short and simple method for the determination of carbon dioxide in calcium carbonate, and all other anhydrous carbonates of the fixed basic elements, is based upon the fact that carbon dioxide is expelled from its combinations when they are fused with vitrified borax. The details of the process are as follows:

Place about 5 grams of borax glass in a platinum crucible, heat it to fusion, cool in a desiccator, and weigh. Then add

about 1 gram of the calcium carbonate and weigh again. The weight of the sample taken and the total weight of crucible, sample, and borax are thus obtained. The sample and borax should be present in about the proportion of 1 : 4 or 1 : 5. Place the crucible over a burner, heat gradually to redness, and maintain this temperature until the contents are in a state of quiet fusion, but avoid excessive heat. Some bubbles of carbon dioxide will remain in the fused mass, but these do not influence the result. Remove the burner, and when the contents of the crucible become solid, place it in a desiccator, allow it to cool, and weigh. The loss in weight is the weight of carbon dioxide, and from this the percentage of carbon dioxide is calculated.

This method yields accurate results if carefully performed. Borax may be fused at a red heat for half an hour without any appreciable loss of weight, but is volatilized quite rapidly at a white heat.

The theoretical composition of calcium carbonate is as follows:

CaO	56.00%
CO_2	44.00%
	100.00%

MANGANOUS CHLORIDE.

22. Determination of Manganese.—Manganese may be determined by several methods, only two of which, one gravimetric and one volumetric, will be given.

1. *Gravimetric Method.*—Dissolve 1 gram of the sample in about 100 cubic centimeters of water in a porcelain dish, heat the solution to boiling, and precipitate the manganese by slowly adding a slight excess of sodium carbonate, while stirring the solution continuously. Continue to boil the solution for a few minutes, and then stand the dish and contents in a warm place for the precipitate to collect and settle. If there is no hurry for the analysis, it is best to let it stand for 12 hours for the last particles of manganese to separate, but this is not necessary, for scarcely any difference

can be observed if it is filtered after standing 2 hours. When the precipitate has completely subsided, decant the clear supernatant liquid through the filter, and wash the precipitate twice by decantation with boiling water. Then bring it on to the filter, and continue to wash with hot water until the precipitate is perfectly clean. Dry the precipitate in an air bath, remove it from the filter as perfectly as possible, and burn the latter in a porcelain crucible. When the crucible cools, add the precipitate, cover the crucible, and ignite moderately; then remove the cover, and ignite intensely until a constant weight is obtained, taking care that only the top of the flame strikes the crucible, in order to prevent the possibility of reducing gases acting on the precipitate. Cool in a desiccator, and weigh as Mn_3O_4, which contains 72.05 per cent. of manganese. From this, calculate the percentage of manganese in the sample.

2. *Volumetric Method.*—Dissolve 1 gram of the sample in about 30 cubic centimeters of water, and from 15 to 20 cubic centimeters of sulphuric acid, made by adding 1 part of concentrate acid to 3 parts of water. Evaporate until all hydrochloric acid is expelled, and heat the residue till dense white fumes of sulphur trioxide are given off. When the residue becomes cool, add 100 cubic centimeters of water, and heat until the residue is completely dissolved. Wash the solution into a liter flask, and nearly neutralize it with a strong solution of sodium carbonate. Add the carbonate until the precipitate at first formed redissolves in the slightly acid solution with difficulty. Then add a slight excess of zinc oxide* suspended in water, shake well, dilute to an exact liter, and again mix the contents of the flask thoroughly. When the precipitate has settled, filter through a dry, folded filter, and receive the filtrate in a dry beaker. Remove 100 cubic centimeters of this solution to a beaker by means of a pipette, add 1 drop of nitric acid of 1.20 Sp. Gr., and heat it to boiling. Remove the flask from the flame, add a little

*Zinc oxide for this purpose is prepared by adding sufficient pure ZnO to water, so that when shaken together, a creamy emulsion is formed.

standard solution of potassium permanganate, replace it over the flame until it just begins to boil, shake quite thoroughly by giving it a rotary motion, and allow the precipitate to settle sufficiently so that the color of the clear supernatant liquid can be seen. If this is clear and colorless, add more permanganate, heat just to boiling, shake, allow the precipitate to settle, and continue this treatment until the clear solution assumes a pink color, due to a slight excess of permanganate.

It is best to use the first 100 cubic centimeters of solution to learn approximately the volume of permanganate used in this titration, and then titrate two or three more quantities, of 100 cubic centimeters each, to get the exact amount of standard solution used. By so doing, nearly the total quantity of permanganate can be added at once, and a more correct result is thus obtained with less trouble and in less time From the mean of two or three titrations, calculate the manganese in 100 cubic centimeters of solution, which represents .1 gram of sample, and from this result calculate the percentage of manganese in the sample.

This method is based upon the fact that when potassium permanganate is added to a neutral, or nearly neutral, solution of manganous sulphate or nitrate, the manganese is precipitated according to the equation:

$$2KMnO_4 + 3MnSO_4 + 2H_2O = 5MnO_2 + 2KHSO_4 + H_2SO_4$$

As soon as all the manganous salt is oxidized, the permanganate colors the solution, and thus indicates the end of the reaction. As 2 molecules of permanganate only oxidize 3 molecules of manganese sulphate, while they oxidize 10 molecules of ferrous sulphate, the oxidizing value of a permanganate solution is only three-tenths as great with respect to manganese as to iron. As the atomic weights of iron and manganese are 56 and 55, respectively, the value in manganese of a solution whose value in iron is known, may be calculated as follows:

$$\tfrac{3}{10} \times \tfrac{55}{56} = \tfrac{165}{560}, \text{ or } .2946.$$

Hence, the value of the permanganate used in iron, multiplied by .2946, gives the value in manganese.

Instead of using either of the methods given, the manganese may be determined as pyrophosphate, by following the directions given in Arts. **36** and **37**, *Quantitative Analysis*, Part 1. It is best, however, to use all of these methods in order to become familiar with them, for all three are largely used in analytical work.

23. Determination of Chlorine.—Weigh about .5 gram of the sample into a beaker, dissolve in 100 cubic centimeters of cold water, precipitate the chlorine with a slight excess of silver nitrate acidified with nitric acid, and proceed with the determination of chlorine, as directed in Art. **12**, *Quantitative Analysis*, Part 1.

24. Determination of Water.—Weigh out from 1 to 2 grams of the pulverized sample, and heat it in an air bath at a temperature ranging from 150° to 175°, until a constant weight is obtained. The sample should be heated for at least an hour before the first weighing. Probably a watch glass is the most convenient vessel in which to dry the sample. The loss in weight is the weight of water expelled by heat, and from this, the percentage of water in the sample is calculated.

The theoretical composition of manganous chloride is as follows:

Mn	27.82%
Cl	35.77%
H_2O	36.41%
	100.00%

COBALTOUS CHLORIDE.

25. Determination of Cobalt.—Dissolve 1 gram of the sample in 150 cubic centimeters of water, heat the solution to boiling, and precipitate the cobalt as hydrate, by slowly adding a slight excess of sodium hydrate to the boiling solution, while stirring continuously. Continue the boiling until the precipitate assumes a brownish-black color, and

becomes of uniform texture. Allow the precipitate to settle, decant the clear liquid through a filter, and wash three or four times with hot water, bringing to boiling and then allowing the precipitate to settle before each decantation. Finally bring the precipitate on to the filter and wash thoroughly with hot water, using a filter pump, if one is at hand. Place the precipitate and filter in a weighed Rose crucible, and ignite moderately with free access of air, until the paper is completely burned. Then, after allowing the crucible to cool, lead in a current of pure hydrogen, and ignite strongly until a constant weight is obtained. The precipitate must be allowed to cool in a current of hydrogen before each weighing. The cobalt hydrate at first formed is converted into oxide when ignited, and this is in turn reduced to metallic cobalt by ignition in hydrogen.

The sodium hydrate clings to the precipitate of cobalt hydrate very tenaciously, but may usually be completely removed by thorough washing with hot water. It is best, however, in order to avoid the possibility of alkali adhering to the metallic residue, to wash this thoroughly with hot water, again ignite, and cool it in a current of hydrogen, and weigh as metallic cobalt. From this weight calculate the percentage of cobalt in the sample.

If nickel is present with cobalt in the sample, these metals must be separated before precipitating the cobalt, or the nickel will also be precipitated and weighed as cobalt. To accomplish this, dissolve the sample in a very small amount of water, and to this concentrate solution add a small excess of potassium hydrate. Then add acetic acid in just sufficient quantity to completely redissolve the precipitate at first formed, stir in a concentrate solution of potassium nitrite that has previously been just acidified with acetic acid, and stand the whole in a warm place for at least 24 hours for the precipitate to collect and settle. The cobalt will be completely precipitated as potassium cobaltic nitrite, while the nickel remains in solution. Filter, and wash the precipitate with a 10-per-cent. solution of potassium acetate in water, to which a little potassium nitrite is added. Dry

the precipitate, remove it as completely as possible from the filter, and burn the latter. Add the precipitate to the ash, and dissolve it in the least necessary quantity of hydrochloric acid. If much acid is used, it must be evaporated nearly to dryness. Dilute the residue to about 50 cubic centimeters, heat to boiling, precipitate the cobalt with sodium hydrate, and proceed as directed above, weighing the cobalt in the metallic state.

26. Determination of Chlorine. — Dissolve about .5 gram of the sample in 100 cubic centimeters of water, precipitate the chlorine as silver chloride, by adding silver nitrate acidified with nitric acid, and proceed as directed in Art. **12**, *Quantitative Analysis*, Part 1.

27. Determination of Water.—Heat about 1 gram of the pulverized sample in an air bath at 150° to 175°, until a constant weight is obtained. From the loss in weight, calculate the percentage of water in the sample, as in the case of manganous chloride.

The theoretical composition of cobaltous chloride is as follows:

Co	35.60%
Cl	42.68%
H_2O	21.72%
	100.00%

AMMONIUM ALUM.

28. Determination of Alumina.—Weigh 1 gram of the roughly pulverized sample into a beaker or porcelain dish, add 100 cubic centimeters of hot water, and stir until the sample is completely dissolved. Add 2 cubic centimeters of concentrate hydrochloric acid, heat the solution to boiling, and precipitate the aluminum by adding a slight excess of ammonium hydrate in small successive portions, while stirring continuously. Continue the boiling a minute or two after precipitation is complete, and then stand aside

for the precipitate to settle. The solution should remain faintly alkaline, but only a very slight excess of ammonia should be present, for any considerable quantity will partially redissolve the precipitate. Decant the clear supernatant liquid through a filter, wash the precipitate once or twice by decantation with about 40 cubic centimeters of hot water, then bring the precipitate on to the filter and wash thoroughly with hot water. The washing is complete when a few drops of the wash water, acidified with nitric acid, give no reaction with silver nitrate, or a few drops, acidified with hydrochloric acid, give no precipitate with barium chloride. Dry the precipitate, fold it in the filter, and ignite, preferably in a platinum crucible, heating gently at first to burn off most of the paper, but finally at the full power of the blast lamp. Cool in a desiccator and weigh as aluminum oxide Al_2O_3. From this weight, calculate the percentage of Al_2O_3 in the sample.

29. Determination of Sulphuric Acid.—Evaporate the filtrate to 150 or 200 cubic centimeters, and if any precipitate separates during the evaporation, filter it off, wash, ignite, weigh, and add this weight to the Al_2O_3 already weighed. When the solution has been sufficiently concentrated, render it slightly acid with concentrate hydrochloric acid, and precipitate the sulphuric acid by adding a small excess of barium chloride to the boiling solution while stirring continuously.

About 15 cubic centimeters of a 10-per-cent. solution is the right amount of reagent to use. Continue the boiling for a few minutes, allow the precipitate to settle, filter, wash, ignite, and weigh, following the directions given in Arts. **66** and **67**, *Quantitative Analysis*, Part 1. From the weight of barium sulphate thus obtained, calculate the percentage of SO_3 in the sample.

Instead of using the filtrate from the alumina for the determination of sulphuric acid, a separate sample of about 1 gram may be dissolved in 150 or 200 cubic centimeters of water, a little hydrochloric acid added, and the sulphuric acid

determined as directed in Art. **66,** *Quantitative Analysis*, Part 1.

30. Determination of Ammonia.—If carefully standardized normal acid and alkali solutions are at hand, proceed with the determination of ammonia exactly as directed in Art. **90,** *Quantitative Analysis*, Part 1, using about 2 grams of the roughly pulverized sample for the determination. The solution is very likely to bump in this case, and it is sometimes necessary to give the flask a rotary motion throughout the entire process.

In case standard acid and alkali solutions are not at hand, substitute dilute hydrochloric acid (about half normal acid is a good strength) for the normal sulphuric acid in the receiver and U tube shown in Fig. 14, *Quantitative Analysis*, Part 1, and proceed to drive over the ammonia exactly as there directed, absorbing it in the hydrochloric acid. Two grams of the alum should be used for this determination, and the flask should be kept in motion, if necessary, to prevent bumping. Although the apparatus is quite rigid, it may be given sufficient motion to prevent bumping. When all the ammonia has been driven over and absorbed in the acid, disconnect the apparatus. Wash the contents of the receiver and U tube into a porcelain dish, and evaporate to dryness on the water bath. Dissolve the residue of ammonium chloride in from 3 to 5 cubic centimeters of water, and precipitate the ammonium with a slight excess of platinum-chloride solution. Place the dish on a water bath and evaporate to a pasty condition without letting the water in the bath come quite to boiling. Remove the dish from the water bath, add about 50 cubic centimeters of 90-per-cent. alcohol, and 15 cubic centimeters of ether, stir the contents of the dish thoroughly, cover it with a watch glass, and let it stand in a cool place for an hour or two. Decant the clear liquid through the asbestos felt in a Gooch crucible which has been previously dried and weighed, wash the precipitate once by decantation with a mixture of 25 cubic centimeters of 90-per-cent. alcohol, and 8 cubic centimeters of ether, and

ɜn wash the precipitate on the felt with the same mixture til all impurities are removed from the precipitate and lt, but avoid excessive washing. Suck the felt as dry as ıssible by means of the filter pump, and then dry the cruci-e and precipitate in an air bath at 130° until a constant eight is obtained. The crucible and contents should be ɜated for an hour before taking the first weighing. The crease in weight is the weight of ammonium-platinum ıloride, and from this weight, the weight of $(NH_4)_2O$ is ılculated by the proportion:

$$(NH_4)_2PtCl_6 : (NH_4)_2O = \text{wt.}\,(NH_4)_2PtCl_6 : x.$$

From the weight thus obtained, the percentage of $(NH_4)_2O$ ı the sample is readily calculated.

Instead of weighing the precipitate in a Gooch crucible, it ıay be filtered and weighed by one of the methods described or the determination of potassium, in Art. **62**, *Quantitative Analysis*, Part 1.

31. Determination of Water.—For the determination of water, weigh out about 1 gram of the roughly pulverized sample, preferably on a watch glass, and heat it in an air bath at 250°, until a constant weight is obtained, heating for about 1 hour before making the first weighing. The loss in weight at this temperature is due to the expulsion of water by the heat, and from this loss in weight, the percentage of water in the sample is calculated. Care must be exercised in making this determination, for, at a little higher temperature, ammonium sulphate will be driven off by heat and calculated as water.

The theoretical composition of ammonium alum is as follows:

Al_2O_3	11.36%
$(NH_4)_2O$	5.73%
SO_3	35.28%
H_2O	47.63%
	100.00%

SEPARATION OF POTASSIUM AND SODIUM.

32. As potassium and sodium must frequently be separated in analysis, it is well to obtain a little practice in making this separation, using a mixture of known composition. This may be done gravimetrically or volumetrically.

GRAVIMETRIC METHOD.

33. Preparation of the Sample.—Weigh accurately about .25 gram of pure sodium chloride, that has been dried at 100°, and cooled in a desiccator, and place it in a small, perfectly clean, porcelain dish. Then weigh out about the same amount of pure potassium chloride, that has been dried and cooled in the same manner, and mix it with the sodium chloride. The combined weight of the two chlorides is the weight of the sample of mixed chlorides taken for analysis.

34. Determination of Potassium.—Dissolve the sample of mixed chlorides in the least necessary quantity of cold water, add a strong solution of platinum chloride that is as nearly neutral as possible, in sufficient quantity to convert all of the sodium and potassium into the corresponding double chloride of platinum and these alkalies, and evaporate almost to dryness on a water bath in which the water is heated almost, but not quite, to boiling. Allow the residue to cool, add about 35 cubic centimeters of 80-per-cent. alcohol, and let it stand in a warm place for an hour or two, stirring occasionally. Decant the liquid through a weighed Gooch crucible, wash the precipitate by decantation with 80-per-cent. alcohol, then transfer it to the asbestos felt in the crucible, and wash with alcohol of the same strength until perfectly clean, but avoid excessive washing. Remove the crucible to an air bath at 130°, until a constant weight is obtained. The crucible should be left in the air bath for an hour before the first weighing. The increase in weight is the weight of potassium-platinum chloride, and from this

the weight of potassium chloride is calculated by the proportion

$$K_2PtCl_6 : 2KCl = \text{wt. } K_2PtCl_6 : x.$$

The weight of KCl thus obtained should, of course, be the weight of KCl taken for analysis.

Instead of weighing the precipitate in a Gooch crucible, a weighed filter may be employed, or it may be weighed in a platinum vessel, by following one of the methods described in Art. **62**, *Quantitative Analysis*, Part 1.

35. Determination of Sodium.—As there is no way to precipitate and weigh sodium, when this method of separation is employed, the sodium is always determined by difference. This is a very simple operation, for, knowing that the original sample contained nothing but the chlorides of sodium and potassium, all that is necessary is to subtract the weight of potassium chloride from the original sample. Hence, in order to obtain the weight of sodium chloride in a mixture of sodium and potassium chlorides, determine the weight of potassium chloride as directed in the preceding article, and subtract this from the weight of the original sample. The result is the weight of sodium chloride.

VOLUMETRIC METHOD.

36. Titration.—Weigh out a sample in the same way that this was done in the last instance, taking about equal quantities of the two chlorides, and having their combined weights amount to from .3 to .5 gram. Place the sample in a beaker or a medium-sized porcelain dish, dissolve in 75 or 100 cubic centimeters of cold water, add a little potassium chromate, and titrate with a standard solution of silver nitrate as directed in Art. **92**, *Quantitative Analysis*, Part 1. From the result thus obtained, calculate the weight of chlorine in the sample. Instead of titrating this solution with silver nitrate, using potassium chromate as an indicator, the weight of chlorine may be determined by Volhard's method (see Art. **104**, *Quantitative Analysis*, Part 1),

using standard solutions of silver nitrate and ammonium sulphocyanide, with iron alum as indicator. From the weight of chlorine obtained by one of these methods, the weight of each of the chlorides is calculated. The calculation follows.

37. Calculation of Results.—The calculation is best explained by means of an example. Let us suppose that .5 gram of the mixed chlorides is taken for analysis, and that the weight of chlorine found by titration is .278 gram:

$$\underset{\text{at.wt.}\,Cl}{35.37} : \underset{\text{mol.wt.}\,KCl}{74.41} = \underset{\text{wt. }Cl}{.278} : x. \quad x = .58485.$$

From this proportion we see that if all the chlorine present were united with potassium, the weight of sample would be .58485 gram, but as the weight of sample taken was .5 gram, part of the chlorine present must be united with sodium, and sodium chloride is present in a quantity proportional to the difference in these weights. The quantity of sodium chloride may be calculated as follows:

The difference between the molecular weights of potassium chloride and sodium chloride (16.04) is to the molecular weight of sodium chloride (58.37) as the difference found (.08485) is to the sodium chloride in the sample.

$$16.04 : 58.37 = .08485 : x.$$
$$x = .3088\ NaCl.$$
$$.5 - .3088 = .1912\ KCl.$$

This indirect method of determining sodium and potassium yields very good results if the quantities of both elements are relatively large, and as the method is rapid and neat, it has much to commend it in such cases. When a relatively large amount of one of the alkalies is mixed with a small quantity of the other, the results obtained are not satisfactory, and in such cases the direct gravimetric method is recommended.

If a standard silver-nitrate solution is not at hand, the sodium and potassium may be determined indirectly by

precipitating the chlorine as silver chloride, as directed in Art. **12,** *Quantitative Analysis*, Part 1, weighing this, calculating the weight of chlorine from the weight of silver chloride, and from this weight, calculating the weights of the two chlorides, in the same way that this was done when the chlorine was determined volumetrically. This method does not yield accurate results when a small amount of one alkali is mixed with a large quantity of the other, and in such cases the direct gravimetric method should be employed.

ALLOYS.

SILVER COINS.

Ag + Cu

38. Silver coins are made of an alloy of silver and copper, usually about 90 per cent. of silver and 10 per cent. of copper, but the proportion in which the two metals are mixed varies somewhat in different countries. A number of methods may be devised for the separation of these metals. A coin, or piece of silverware, is usually analyzed by successively precipitating the silver and copper from a solution of the sample and weighing the precipitates in the usual manner, but these metals may be separated by electrolysis, and on account of the constantly increasing importance of the electrolytic methods, the student is strongly advised to make at least one determination by each method, for this is a very good analysis for practice.

THE ORDINARY METHOD.

39. Determination of Silver.—Dissolve between .5 and 1 gram of the sample in dilute nitric acid in a small porcelain dish, and evaporate the solution over a water bath until the residue solidifies, but remains slightly soft and moist.

Dissolve this residue in a little hot water, wash it into a beaker, and rinse out the dish, adding the washings to the solution in the beaker until this solution amounts to about 75 cubic centimeters. Heat the solution moderately, and precipitate the silver as chloride by gradually adding a slight excess of dilute hydrochloric acid while stirring the solution constantly. When a slight excess of the reagent has been added, increase the temperature and stir frequently, until the solution begins to boil, and the precipitate gathers together and settles readily. As soon as the precipitate settles, filter, and wash it thoroughly with hot water, taking care not to lose any of the filtrate or washings. Dry the precipitate, remove it as completely as possible from the filter, and burn the latter in a porcelain crucible. Add 3 or 4 drops of nitric acid and 2 drops of hydrochloric acid to the ash in the crucible, evaporate to dryness, add the main precipitate, ignite cautiously, cool in a desiccator, and weigh as silver chloride, following the directions given in Art. **30**, *Quantitative Analysis*, Part 1. From this weight, calculate the percentage of silver in the sample in the usual manner.

40. Determination of Copper.—The copper in the filtrate is probably determined as sulphide more often than in any other way, but it may also be determined as oxide, or as metallic copper, by means of electrolysis. The methods are as follows:

1. *Determination as Sulphide.*—Evaporate the filtrate and washings to about 100 cubic centimeters, taking care not to lose any of the solution; cover the beaker to exclude the air as much as possible, and conduct a current of hydrogen sulphide through the solution, while keeping it as near the boiling point as possible, until the copper is completely precipitated and the solution smells strongly of the precipitant. As soon as the precipitate settles, filter as rapidly as possible, preferably with the aid of a filter pump, and wash without interruption with water containing hydrogen sulphide. Dry the precipitate, burn the filter, add a little sulphur to the precipitate, and ignite it in a Rose crucible in

a current of pure hydrogen, as directed in Arts. **18** and **19,** *Quantitative Analysis*, Part 1, which should be read in connection with this determination. From the weight of cuprous sulphide Cu_2S thus obtained, calculate the percentage of copper in the sample.

As copper sulphide readily oxidizes to copper sulphate, when exposed to the action of air, the precipitate should be protected from the air as much as possible, and the filtration and washing should be accomplished in the least necessary time. In igniting the precipitate, care must be taken to have all the air expelled from the generator and crucible by the hydrogen, before applying heat, or an explosion will result. The whole operation should be carried through as rapidly as possible.

2. *Determination as Oxide.* — Concentrate the filtrate from the silver to about 200 cubic centimeters, wash it into a porcelain dish, and heat it over a Bunsen burner. To the gently boiling solution, slowly add a slight excess of sodium hydrate, while stirring continuously, and continue the boiling until the precipitate becomes black, and of uniform texture. Allow the precipitate to settle, wash it two or three times by decantation with hot water, and then wash it thoroughly on the filter with hot water. Dry the precipitate, remove it as completely as possible from the filter, and burn the latter in a porcelain crucible. Moisten the ash with 2 or 3 drops of nitric acid, and evaporate to dryness. Then add the precipitate, ignite at the highest temperature of the Bunsen burner, cool, and weigh, as directed in Art. **16,** *Quantitative Analysis*, Part 1. The precipitate is copper oxide CuO, and from its weight, the percentage of copper is calculated in the usual manner.

3. *Determination as Metallic Copper, by Electrolysis.*— To the filtrate from the silver, add 3 or 4 cubic centimeters of concentrate sulphuric acid, and evaporate until the residue becomes pasty. Then heat the residue until white fumes of SO_3 are given off, thus expelling all hydrochloric acid. Add about 1 cubic centimeter of dilute nitric acid, dilute to 150 cubic centimeters, and deposit the copper by means of

an electric current, following the directions given in Art. **20**, *Quantitative Analysis*, Part 1. When the copper is all deposited, disconnect the apparatus, wash the negative electrode containing the copper by dipping it successively in three or four beakers of hot water, and finally in a beaker of alcohol, dry it quickly, and weigh as soon as cool. From the weight of copper thus obtained, calculate the percentage of copper in the sample.

The filtrate from the silver is evaporated to dryness with the addition of sulphuric acid, in order to expel all the hydrochloric acid, and as this acid interferes with the deposition of copper by electrolysis, this operation should not be neglected if accurate results are required. By using only a slight excess of dilute hydrochloric acid in precipitating the silver, and exercising care throughout the entire analysis, the writer has obtained very satisfactory results by electrolyzing the filtrate, without first expelling the small amount of hydrochloric acid present.

SEPARATION BY ELECTROLYSIS.

41. Determination of Silver.—Dissolve about .5 gram of the sample in a small quantity of dilute nitric acid, and evaporate almost to dryness on the water bath in order to remove the excess of acid. While this is evaporating, dissolve 5 or 6 grams of potassium cyanide in 150 or 200 cubic centimeters of water, and dissolve the residue, consisting of the nitrates of silver and copper, in this solution. Connect with a battery and electrolyze this solution, using a current that gives from .2 to .8 cubic centimeter of electrolytic gas (oxygen and hydrogen) per minute.* The potassium cyanide holds the copper in solution, but the silver begins to deposit at once. If the operation is carried out in the cold, it will take about 24 hours to completely precipitate the silver, but

* Probably the best way to measure an electric current is to pass it through sulphuric acid of 1.22 Sp. Gr., in an apparatus similar to that shown in Fig. 14, *Inorganic Chemistry*, Part 1. The electrolytic gas evolved in a given time is collected over water and measured in a eudiometer.

the operation can be shortened to about 12 hours by heating the solution to 65° while the current is passing through it. When the silver is completely deposited, disconnect, wash, dry, and weigh the electrode, just as in the determination of copper (see Art. **20**, *Quantitative Analysis*, Part 1), and from the weight of silver thus obtained, calculate the percentage of silver in the sample.

42. Determination of Copper.—As soon as the silver is determined, connect the apparatus again, and through the solution containing the copper pass a current giving about 3 cubic centimeters of electrolytic gas per minute. This will decompose the potassium cyanide, and as soon as the excess of cyanide is decomposed, the copper will commence to separate on the negative electrode in a dense bright coating. The copper will be completely precipitated in a few hours. Wash the electrode by dipping it in hot water and alcohol in the usual manner, dry it in an air bath, and weigh as soon as cool. From the weight of copper thus obtained, calculate the percentage of copper in the sample.

BRASS.

$$Cu + Zn + (Pb)$$

43. Brass is essentially an alloy of copper and zinc, but as much of the brass of commerce also contains some lead, a careful qualitative analysis should precede the quantitative examination, and the method adopted should depend upon what we learn from this examination. If the sample contains lead, the following method is recommended.

44. Determination of Lead. — Weigh out from .6 to 1 gram of the sample, and dissolve it in a slight excess of half-strength nitric acid. When solution is complete, heat gently until nitrous fumes cease to be evolved. Then add a little dilute sulphuric acid (from 5 to 10 cubic centimeters, according to the size of the sample) and evaporate to dryness on the water bath. When dry, remove to a tripod,

and heat cautiously over a burner until white fumes of sulphuric acid begin to be given off. After the residue has become cool, add about 150 cubic centimeters of cold water, and allow it to stand for half an hour, stirring frequently until the precipitate is perfectly white. Filter off the lead sulphate, and wash it with water containing a little sulphuric acid, until the other metals are completely removed from the precipitate and filter, taking care not to lose any of the filtrate or washings. Now remove the filtrate from under the funnel, and wash with dilute alcohol until all the sulphuric acid has been removed from the precipitate and filter. These washings may be thrown away, as they contain no metallic element. Dry the precipitate, remove it from the paper, burn the filter, convert any reduced lead to sulphate, add the precipitate, ignite gently, cool in a desiccator, and weigh as lead sulphate. From this weight, calculate the percentage of lead in the sample. Arts. **26** and **27**, *Quantitative Analysis*, Part 1, should be read in connection with this determination.

45. Determination of Copper.—Evaporate the filtrate and washings from the lead determination to about 150 cubic centimeters, or, if a qualitative examination shows that the sample does not contain lead, omit all the preceding, evaporate the original solution to dryness, without the addition of sulphuric acid, and dissolve the residue in about 150 cubic centimeters of water. In either case, add a gram of potassium nitrate to the solution, and separate the copper from the solution by electrolysis, as directed in Art. **20**, *Quantitative Analysis*, Part 1. As soon as the solution becomes colorless, a drop of it should be removed to a porcelain plate, and mixed with a drop of hydrogen sulphide, and this should be repeated at frequent intervals until a black precipitate is no longer formed when the two liquids are mixed. The amount of zinc lost in thus testing is not appreciable. As soon as the copper is completely deposited, as indicated by the absence of a black precipitate when drops of the two liquids are mixed, the apparatus should be disconnected, as

a small quantity of zinc is likely to be deposited on the electrode with the copper, if the current is allowed to pass through the solution after all the copper is deposited. Remove the electrodes from the solution, and while holding them over the beaker, rinse them off by means of a wash bottle, allowing the washings to run back into the main solution, and thus avoiding loss of liquid containing zinc. Then wash the negative electrode in the usual manner, by dipping it successively into several beakers of hot water, and finally into a beaker of alcohol. Dry, cool, and weigh the electrode as rapidly as possible to prevent oxidation of the copper. The increase in weight is the weight of copper in the sample, and from this the percentage of copper is calculated.

46. Determination of Zinc.—Heat the solution, from which the copper has been removed by electrolysis, to boiling, and precipitate the zinc by adding a slight, but distinct, excess of sodium carbonate, in small successive portions, while stirring the solution continuously. After adding a slight excess of sodium carbonate, continue the boiling for 15 minutes to complete the precipitation of the zinc. Allow the precipitate to settle completely, decant the clear liquid through a filter, and wash once or twice by decantation with hot water. Then transfer the precipitate to the filter, and wash with hot water until all impurities are removed, but avoid excessive washing. Dry the precipitate, remove it as completely as possible from the filter, and burn the paper at as low a temperature as possible. When the crucible cools, add the precipitate and ignite, gently at first, but gradually increasing the temperature, and finally igniting for 10 minutes at the highest temperature of the Bunsen burner. Cool in a desiccator, weigh as zinc oxide ZnO, and from this weight, calculate the percentage of zinc in the sample. In connection with this determination, the student should read Arts. **50** and **51**, *Quantitative Analysis*, Part 1.

47. Estimation of Copper and Zinc as Sulphides.—The writer prefers the method just given for the separation

of copper and zinc, but they are often successively precipitated from their solution as sulphides, and weighed as such. This method is handy in case a battery is not at hand. The details of the process are as follows:

The solution of the sample, which does not contain lead, is evaporated to dryness on the water bath, and the residue dissolved in about 100 cubic centimeters of water, or the solution from which the lead has been separated is evaporated to about the same volume. In either case, add 5 or 6 cubic centimeters of concentrate hydrochloric acid, heat the solution to boiling, and while keeping it just at the boiling point, or as near this temperature as possible, precipitate the copper by leading hydrogen sulphide through the solution at the rate of three or four bubbles per second. The beaker should be covered to protect the contents from the air as much as possible during precipitation. The copper sulphide thus precipitated, even in the presence of considerable hydrochloric acid, will carry some zinc sulphide with it, and in order to render the separation complete, reprecipitation must be resorted to. The precipitate will settle rapidly, and as soon as it has completely subsided, filter, and wash five or six times on the paper with water containing hydrogen sulphide. Stand the filtrate aside for further treatment. Transfer the precipitate from the filter to a porcelain dish, and dissolve it in the least necessary quantity of aqua regia, and evaporate to dryness on the water bath. Dissolve the residue in about 100 cubic centimeters of water and 5 or 6 cubic centimeters of concentrate hydrochloric acid, heat the solution to boiling, and again precipitate the copper by a current of hydrogen sulphide in the same way that this was done in the first instance. The small quantity of zinc that was carried down with the copper in the form of sulphide, in the first instance, will now remain in solution.

As soon as the precipitate settles, filter, and wash it without interruption with water containing a little hydrogen sulphide, taking care not to lose any of the filtrate. Dry the precipitate, remove it from the paper, burn the filter in a Rose crucible, add the precipitate, sprinkle a little flowers of sulphur

over it, and ignite in a current of hydrogen, as directed in Arts. **18** and **19,** *Quantitative Analysis*, Part 1. Pass the hydrogen through the crucible until it is almost cool, then remove it to a desiccator and allow it to become perfectly cool. Weigh the precipitate as cuprous sulphide Cu_2S, and from this, calculate the percentage of copper in the sample.

As it is almost impossible to transfer all of the precipitate from the filter to a dish, it is always best, after removing as much of the precipitate as possible, to dry and burn the filter, and add the ash to the precipitate before dissolving it in aqua regia for the second precipitation.

Unite the two filtrates, which contain all the zinc, and evaporate this solution to about 150 cubic centimeters. Add ammonia enough to render the solution distinctly alkaline, and then to the gently boiling solution, add ammonium sulphide in small, but distinct, excess. When sufficient reagent has been added to completely precipitate the zinc, stir well, cover the beaker, and stand in a warm place until the precipitate subsides. Wash the precipitate once by decantation with hot water containing a little ammonium sulphide and ammonium chloride, and then wash on the filter with hot water containing a little ammonium sulphide, but avoid excessive washing. Dry the precipitate, remove it to a watch glass, burn the filter in a Rose crucible, add the precipitate, sprinkle a little sulphur over it, and ignite for 10 minutes at the highest temperature obtainable with a Bunsen burner. A blast lamp should not be used. Allow the precipitate to cool in a current of hydrogen, and weigh as zinc sulphide ZnS. Arts. **54** and **55,** *Quantitative Analysis*, Part 1, should be read in connection with this determination.

BRONZE.

$$Cu + Sn + (Pb)$$

48. Bronze is an alloy of copper and tin, but some samples contain other metals, especially lead. A careful qualitative analysis of the sample should first be made, and the

method of analysis adopted should depend upon what this examination shows. As a rule, probably only tin and copper will be found, and, when such is the case, the method given below is recommended.

ALLOY OF COPPER AND TIN.

49. Determination of Tin.—Weigh out, accurately, from .5 to 1 gram of the sample, which should be in a finely divided condition; transfer it to a porcelain dish that is covered with a watch glass, and add enough half-strength nitric acid to decompose it, but avoid much excess of acid. When the action has nearly ceased, place the dish on a water bath, and evaporate the solution to dryness. To the solid residue, add concentrate hydrochloric acid drop by drop until it is thoroughly moistened, but take care not to add much more than is necessary to moisten the residue, for if enough is added so that there is any considerable quantity of free fluid present, it will hold some of the tin in solution and thus vitiate the results. After moistening the residue with hydrochloric acid, allow it to stand for half an hour; then add about 100 cubic centimeters of water and heat gently. The solid matter will now usually dissolve as cupric and stannic chlorides, but if a small quantity of stannic oxide remains undissolved, it makes no difference. To the solution add from 10 to 20 cubic centimeters of dilute sulphuric acid, according to the weight of sample taken, dilute to about 200 cubic centimeters, boil for a few moments, and stand aside for 10 or 12 hours for the precipitate to completely separate and settle. Filter, and wash three times with hot water, nearly filling the filter with water each time, and taking care to direct the stream from the wash bottle around the top of the paper. Now remove the filtrate, which will contain all the copper, and stand it aside for the determination of copper. Place another beaker under the funnel, and continue to wash the precipitate with hot water until the washings give no precipitate with silver nitrate. These washings do not contain copper, and may be thrown away.

Dry the precipitate, remove it as completely as possible to a watch glass, cautiously burn the filter in a porcelain crucible, and heat the residue with a few drops of nitric acid to oxidize any tin that may be reduced. When the crucible becomes cool, transfer the precipitate to it, add a little ammonium carbonate, and ignite at the highest temperature of the Bunsen burner. When the crucible has partly cooled, add a little more ammonium carbonate, and again ignite. Repeat this several times to remove most of the sulphuric acid, then ignite intensely over the blast lamp with the addition of a little ammonium carbonate, and continue this treatment until a constant weight is obtained. The precipitate is stannic oxide SnO_2, and from its weight, the percentage of tin in the sample is calculated. SnO_2 contains 78.67 per cent. of tin.

50. Determination of Copper.—The copper in the filtrate may be determined in three different ways. The filtrate is evaporated to about 100 cubic centimeters, and one of the following methods is applied.

1. Heat the solution to boiling, precipitate the copper with a slight excess of sodium hydrate, and continue the boiling until the precipitate becomes uniform. Filter, wash, dry, ignite, and weigh as directed in Art. **16**, *Quantitative Analysis*, Part 1. From the weight of copper oxide CuO thus obtained, calculate the percentage of copper in the sample.

2. Deposit the copper on a weighed negative electrode by means of a battery. Wash, dry, cool, and weigh, following the directions given in Art. **20**, *Quantitative Analysis*, Part 1. The increase in weight is the weight of copper in the sample, and from this, the percentage of copper is calculated.

3. Acidify the solution with 1 or 2 cubic centimeters of concentrate hydrochloric acid, heat it to boiling, and precipitate the copper as sulphide, by leading a rather rapid current of hydrogen sulphide through the solution. The solution should be protected from the air during precipitation, and

this is best accomplished by passing the tube that leads the hydrogen sulphide into the solution through a perforation in the watch glass placed over the beaker. As soon as the precipitate settles, filter, and wash with water containing hydrogen sulphide. Filtration and washing should be accomplished as rapidly as possible. A filter pump may be used in this determination, but strong suction should be avoided, and as soon as one lot of wash water runs through, another lot should be added to protect the precipitate from the air. Dry the precipitate, ignite it, with the addition of sulphur, in a current of hydrogen, and weigh as cuprous sulphide Cu_2S, following the directions given in Arts. **18** and **19**, *Quantitative Analysis*, Part 1.

ALLOY OF COPPER, TIN, AND LEAD.

51. Determination of Tin.—If the bronze contains lead, the method just described cannot be employed, for the lead and tin would be precipitated together by the sulphuric acid. In this case, place from .5 to 1 gram of the finely divided sample in a covered porcelain dish, and add enough nitric acid of 1.3 Sp. Gr. to completely decompose it. When the action ceases, place the dish on a water bath and evaporate to dryness. After all the nitric acid has been expelled, allow the residue to cool, moisten it with a few drops of nitric acid having the same strength as that used in decomposing the sample, and add about 100 cubic centimeters of water. Heat the solution almost to boiling, stir it well, and allow the precipitate to settle completely. Filter, and wash the precipitate with hot water until the washings scarcely redden blue litmus paper, taking care not to lose any of the filtrate or the first of the washings. A few drops of wash water from the third or fourth portion added, taken to test with litmus paper, will have no effect on the result. Dry the precipitate, remove it to a watch glass, burn the filter in a porcelain crucible, add a few drops of nitric acid to convert any tin, that may have been reduced while burning the paper, back to oxide, and evaporate to dryness. Add the precipitate, and ignite,

gently at first, but finally for 5 minutes at the full power of the blast lamp. Cool in a desiccator, and weigh. If the precipitate is white, it consists of stannic oxide SnO_2, and the percentage of tin may be calculated from this weight. If, however, the precipitate is colored, it contains more or less copper oxide, and a correction must be made. This is done as follows:

To the precipitate in the porcelain crucible, add five or six times its weight of a mixture containing equal parts of dry sodium carbonate and sulphur, and heat until the contents of the crucible are in a state of quiet fusion. Allow the fusion to cool, and treat the residue with hot water until the tin dissolves as sodium sulphostannate Na_2SnS_3 and leaves the copper precipitated as sulphide. After making sure that all tin has gone into solution, filter off the copper sulphide, wash it rapidly with hot water containing hydrogen sulphide; dry, burn the filter, add the precipitate and a little sulphur, ignite in a current of hydrogen, cool, and weigh as cuprous sulphide Cu_2S. Note this weight and add it to the weight of cuprous sulphide obtained later in the determination of copper. On account of the relation of the atomic weights, the weight of copper oxide mixed with the stannic oxide is the same as the weight of cuprous sulphide found. Hence, subtract this weight from the weight of the mixed oxides, and from the result, calculate the percentage of tin in the sample. The percentage of tin in stannic oxide is usually given as 78.67.

52. Determination of Lead.—To the filtrate from the tin, add about 10 cubic centimeters of dilute sulphuric acid, and evaporate the solution until white fumes of SO_3 begin to be driven off. Allow the residue to cool, add about 100 cubic centimeters of water, stand it aside for at least half an hour, and stir frequently until the precipitate is perfectly white. Filter, and wash with water containing a little sulphuric acid until the copper is completely removed from the precipitate and filter. Then remove the filtrate, stand it aside for the determination of copper, place another beaker under

the funnel, and wash with dilute alcohol until the sulphuric acid is removed from the precipitate and filter. As these washings do not contain copper, they may be thrown away. Dry the filter and precipitate and proceed with the determination of lead by one of the methods described in Arts. **26** and **27**, *Quantitative Analysis*, Part 1.

Instead of evaporating the solution almost to dryness after adding sulphuric acid, the lead may be determined by evaporating to about 100 cubic centimeters, adding 10 cubic centimeters of dilute sulphuric acid to the moderately warm solution, stirring well, allowing the solution to stand for several hours for the precipitate to collect and settle, filtering and proceeding as above, but the first method is recommended.

53. Determination of Copper.—Evaporate the filtrate, from which the lead has been separated, to about 100 cubic centimeters, precipitate the copper as oxide, sulphide, or as metallic copper, by one of the methods given in Art. **40**, and from the weight of the precipitate obtained, added to the weight of copper separated from the tin precipitate, calculate the percentage of copper in the sample. If the copper is precipitated as sulphide or oxide, the weights of the two precipitates may be added. Otherwise the weight of copper in the first precipitate must be calculated and added to the weight of copper in the second.

TYPE METAL.

$Sb + Pb$

54. Determination of Lead. — Dissolve from 2 to 3 grams of tartaric acid in the least necessary quantity of water so as to get a saturated solution, and to this add an equal volume of concentrate nitric acid. Then weigh out from .6 to 1 gram of the finely divided sample, add it to the mixture of acids and stir with a glass rod till the sample is completely dissolved, applying gentle heat if necessary. It

is often a difficult matter to dissolve this alloy, and if the sample is not finely divided there is much danger of failure. Usually, solution is best accomplished by adding the finely divided sample to about three times its weight of solid tartaric acid dissolved in the least necessary quantity of water and mixed with an equal volume of concentrate nitric acid, but sometimes a slightly different proportion appears to be better. When all is dissolved, dilute the solution to from 75 to 100 cubic centimeters, and precipitate most of the lead with a slight excess of dilute sulphuric acid. Allow the precipitate to settle, and filter, receiving the filtrate in a porcelain dish. When the liquid has all run through the filter, stand the filtrate aside, place a beaker or second porcelain dish under the funnel, wash the precipitate thoroughly with pure water, and dry it in an air bath. Evaporate the washings to a very small bulk, and add this solution to the filtrate in the porcelain dish. The solution thus obtained will contain all the antimony, and a little lead that was not separated by the sulphuric acid. To this solution, add ammonium hydrate until it is distinctly alkaline, and then add an excess of ammonium sulphide and boil for 5 minutes. This will at first precipitate all of the lead and part of the antimony as sulphides, but upon heating, the antimony will all go into solution in the excess of ammonium sulphide, as ammonium sulphantimonite $(NH_4)_3SbS_3$, while the lead will remain undissolved, as black lead sulphide PbS. Allow the precipitate to settle, decant the clear liquid through a filter, add a little more ammonium sulphide to the precipitate, and digest it on a water bath for 10 or 15 minutes. Then bring the precipitate on to the filter, wash thoroughly with pure water, and dry it in the air bath. Remove the precipitates of lead sulphate and sulphide to separate watch glasses, and burn the filters together in a porcelain crucible. When the crucible becomes cool, brush in the precipitate of lead sulphide, add 5 or 6 drops of nitric acid and 2 drops of sulphuric acid, and evaporate to dryness. If the precipitate is not white now, the treatment with acids must be repeated. The precipitate of sulphide, and the lead that was reduced in

burning the filters, will now be converted into sulphate. After allowing the crucible to cool, add the precipitate of lead sulphate, cover the crucible, heat to low redness over a Bunsen burner for 5 minutes, cool in a desiccator, and weigh as lead sulphate. From this weight, calculate the percentage of lead in the sample.

55. Determination of Antimony.—To the alkaline filtrate from the lead sulphide, add dilute hydrochloric acid until the solution has a distinct acid reaction, but avoid a large excess of acid. This will precipitate the antimony as sulphide, together with some free sulphur. Heat the solution and precipitate on the water bath until the hydrogen sulphide is completely expelled. The removal of the hydrogen sulphide may be hastened by leading a current of carbon dioxide through the hot solution. When the solution no longer smells of hydrogen sulphide, filter through a paper that has been dried at a temperature ranging from 100° to 110° and weighed between matched watch glasses; wash the precipitate thoroughly with hot water, remove precipitate and filter to an air bath, dry it at the same temperature that was employed in drying the filter alone, and weigh between matched glasses. As the weight always changes quite rapidly in these cases, the weighings should be made in as nearly the same time, and under as nearly the same conditions as possible. The increase in weight over the weight of the paper alone is the weight of the precipitate. This consists of a variable mixture of antimony sulphide, sulphur, and water, and a correction must be made either by heating in a current of carbon dioxide, or by treating with fuming nitric acid, following the directions given in Arts. **60** and **61**, *Quantitative Analysis*, Part 1, in either case. If the precipitate is large enough, it is best to treat separate portions of it by each method, and take the mean of the results calculated by these two methods as the weight of antimony sulphide. From this weight, calculate the percentage of antimony in the sample.

Instead of weighing the lead as sulphate after separating

most of it by means of sulphuric acid, it is sometimes precipitated as sulphide by adding ammonium sulphide to the alkaline solution, and weighed as such after igniting in a current of hydrogen. This method is not advised, however, for when a large amount of lead is precipitated as sulphide from a solution that also contains antimony, some of the antimony is invariably precipitated with the lead. This difficulty is obviated by precipitating most of the lead as sulphate, and then precipitating the small amount that remains as sulphide, as directed in the first instance.

SOFT SOLDER OR PEWTER.

Sn + Pb

56. Determination of Tin.—Weigh out about .5 gram of the finely divided sample, and cautiously add sufficient nitric acid of 1.3 Sp. Gr. to completely decompose it. When the action nearly ceases, evaporate the solution to dryness on the water bath. Add a few drops of nitric acid to the residue, then add about 100 cubic centimeters of water, heat almost to boiling, allow the precipitate to settle, and filter. Wash the precipitate thoroughly with hot water, and dry it in the air bath. Remove the precipitate to a watch glass, and cautiously burn the filter in a porcelain crucible, using as little heat as possible. To the ash, add a few drops of nitric acid of 1.3 Sp. Gr. to oxidize any tin that may have been reduced while burning the paper, and evaporate to dryness. When the crucible cools, add the precipitate, heat, gently at first, but finally ignite strongly over the blast lamp for 5 minutes, cool in a desiccator, and weigh. The precipitate, which consists principally of stannic oxide, will nearly always contain some lead, and a correction must be made.

To do this, mix the precipitate in the porcelain crucible with five or six times its weight of a mixture of equal parts of dry sodium carbonate and flowers of sulphur, and heat

at a moderate temperature over a blast lamp, or at the highest power of a Bunsen burner, until the contents of the crucible are in a state of quiet fusion. Cool the crucible, and digest the fused residue with water, stirring frequently, until the tin is completely dissolved as sodium sulphostannate Na_2SnS_3, and the lead remains as black insoluble sulphide PbS. Filter off the lead sulphide, wash it thoroughly with hot water, and dry it in an air bath. Remove the precipitate as completely as possible from the filter, and burn the latter in a porcelain crucible, using as little heat as possible. When the crucible is cool, add the precipitate, moisten it with 5 or 6 drops of nitric acid, add 2 drops of concentrate sulphuric acid, and evaporate to dryness. If this does not render the precipitate white, the treatment with acids must be repeated until it is white. Then ignite it gently over a Bunsen burner, cool in a desiccator, and weigh as lead sulphate. Note this weight and add it to the weight of lead sulphate obtained later, in the determination of lead.

From the weight of lead sulphate thus obtained, calculate the weight of lead oxide that was mixed with the stannic oxide, and subtract this weight from the weight of the original precipitate. The result is the weight of stannic oxide SnO_2, and from this weight, the percentage of tin in the sample is calculated.

57. Determination of Lead.—To the filtrate from the stannic oxide, add dilute sulphuric acid in moderate excess, and evaporate on the water bath until all the nitric acid is expelled. The appearance of the residue at this point will depend upon the amount of sulphuric acid added. If only a slight excess is present the residue will be almost dry, but if more has been added it will remain mixed with the residue, as the heat of the water bath is not sufficient to expel it. A moderate excess of acid does no harm, but a large excess should be avoided. It is a good plan to remove the residue from the water bath, and heat it gently over a Bunsen burner until fumes of SO_3 begin to be given off, but this is

unnecessary if evaporation on the water bath is continued until certain that all nitric acid is expelled.

After the residue is cool, add 50 cubic centimeters of cold water, stir well, and then add an equal amount of 95-per-cent. alcohol, and allow to stand for half an hour while stirring frequently. Allow the precipitate to settle, filter through an asbestos felt in a porcelain Gooch crucible that has been previously dried and weighed, wash thoroughly with half-strength alcohol, and dry in an air bath at 130°. Cool the crucible and precipitate in a desiccator, and weigh as lead sulphate. The porcelain crucibles of Gooch's form do not have a cap to fit over the bottom, but as the precipitate does not come in contact with reducing gases in this operation, this does not matter.

The porcelain Gooch crucible is very handy in this determination, but if one is not available, a weighed filter may be substituted, or the precipitate may be filtered, washed, dried, ignited, and weighed in the ordinary manner, following the directions given in Arts. **26** and **27**, *Quantitative Analysis*, Part 1. In any case, add to the weight of this precipitate the weight of lead sulphate separated from the stannic oxide, and from the resulting weight, calculate the percentage of lead in the sample.

NICKEL COINS.

$$Cu + Ni + (Co + Fe)$$

58. Nickel coins are made from an alloy of copper and nickel, but they frequently contain weighable quantities of iron and cobalt as impurities. They are usually analyzed by successively separating the metals from a solution by means of reagents, but if the coins are pure, they may be completely analyzed by means of the electric current, as in the case of silver coins, and the analysis may be largely performed by means of electrolysis in any case. The ordinary method and the electrolytic separation are both given, and the student is advised to make at least one analysis each way.

THE ORDINARY METHOD.

59. Determination of Copper.—Dissolve from .5 to 1 gram of the sample in a little dilute nitric acid, and evaporate to dryness on the water bath. Moisten the residue with 3 or 4 cubic centimeters of concentrate hydrochloric acid, and dissolve it in 100 cubic centimeters of water. Heat this solution to boiling, cover the beaker, and precipitate the copper by passing a rather rapid current of hydrogen sulphide through the hot solution. Filter as soon as the precipitate settles, and wash thoroughly on the filter with water containing hydrogen sulphide. Dry the precipitate, ignite it with the addition of sulphur, in a current of hydrogen, weigh as cuprous sulphide Cu_2S, and from the weight thus obtained, calculate the percentage of copper in the sample. Arts. **18** and **19**, *Quantitative Analysis*, Part 1, should be read in connection with this determination, and the directions there given should be closely followed.

60. Determination of Nickel.—Boil the filtrate from the copper until the hydrogen sulphide is all expelled and the solution is evaporated to about 150 cubic centimeters. Wash this solution into a porcelain dish, heat it to boiling, precipitate the nickel with a moderate excess of sodium hydrate, and continue the boiling. After a few minutes, add bromine water to this boiling solution, in small successive quantities, while stirring continuously, until the precipitate becomes black and of uniform texture. The solution must be kept slightly alkaline throughout the operation. Wash the precipitate three or four times by decantation with hot water, and then wash on the filter with hot water until the last trace of alkali is removed. Dry the precipitate, and proceed according to one of the following methods. If a qualitative analysis has shown that the sample contains only copper and nickel, the first method is recommended, but if iron or cobalt is present, the second method is better.

1. Remove the precipitate from the filter, and burn the

latter in a weighed porcelain crucible. Add 2 or 3 drops of nitric acid to the ash, and cautiously evaporate to dryness. Then add the precipitate, ignite strongly, cool in a desiccator, and weigh as nickel oxide *NiO*. From this weight, calculate the percentage of nickel in the sample.

2. Burn the filter in a weighed Rose crucible, allow the crucible to cool, add the precipitate, lead in hydrogen, and when the air has all been expelled by the hydrogen, ignite as in the determination of copper as sulphide (see Art. **18**, *Quantitative Analysis*, Part 1), until a constant weight is obtained. The precipitate must be allowed to cool in the current of hydrogen before each weighing. The nickel will now be in the metallic condition, and if cobalt and iron are present, they will also be in the metallic state. If the precipitate is pure nickel, the percentage of nickel in the sample may be calculated directly from this weight, but if iron or cobalt is present, a correction must first be made. This is done as follows:

Dissolve the metallic residue that has just been weighed in a small quantity of nitric acid, nearly neutralize the solution with ammonium hydrate, and then add an excess of ammonium carbonate. This will precipitate the iron as hydrate, while the cobalt and nickel at first precipitated dissolve in the excess of reagent. After digesting on the water bath for some time, filter, and wash two or three times on the filter with hot water. Then dissolve the precipitate on the filter, by pouring a little warm dilute hydrochloric acid over it. Wash the filter once with water, then pour a little more dilute hydrochloric acid over it, and wash twice more with water, receiving the solution and washings in a clean beaker. Nearly neutralize the solution with ammonium hydrate, and again precipitate the iron with an excess of ammonium carbonate. Digest on the water bath for about half an hour, filter, wash once with hot water, and then add this filtrate to the original filtrate and set it aside for further treatment. Then continue to wash the precipitate of ferric hydrate with hot water, until it is perfectly clean. Fold the filter around the precipitate, place it in a weighed crucible,

ignite gently at first, and then raise the temperature and ignite at the full power of the blast lamp for several minutes. Cool the crucible and precipitate in a desiccator, and weigh as ferric oxide Fe_2O_3. From this weight, calculate the weight and percentage of iron in the sample.

The filtrate from the iron contains the nickel and cobalt. Evaporate this solution to dryness, and heat the residue cautiously to expel ammonium salts. When cool, add a little hydrochloric acid, and a few drops of nitric acid to the residue, and dissolve it in a few cubic centimeters of water. Render this solution alkaline with potassium hydrate, and then add just enough acetic acid to completely dissolve the precipitate produced by the potassium hydrate. To this solution, add a concentrate solution of potassium nitrite, aciduiated with acetic acid, stir well, and stand in a warm place for 24 hours. The cobalt will now be completely precipitated as yellow potassium cobaltic nitrite, while the nickel remains in solution. Filter, and wash the precipitate well with a 10-per-cent. solution of potassium acetate, to which a little potassium nitrite is added. Dry the precipitate, remove it as completely as possible from the filter, and burn the latter. Add the precipitate to the ash, and dissolve it in the least necessary quantity of hydrochloric acid. Dilute the solution to about 50 cubic centimeters, heat to boiling, precipitate the cobalt with a slight excess of sodium hydrate, and continue the boiling until the precipitate becomes black and of uniform texture. Filter, using a pump if one is at hand, wash thoroughly with hot water, and suck the precipitate and filter as dry as possible by means of the pump. Fold the filter around the precipitate, and ignite in a Rose crucible to burn the paper; then ignite the precipitate in a current of hydrogen, and weigh as metallic cobalt. From this, calculate the percentage of cobalt in the sample, then add the weights of cobalt and iron, subtract this from the weight of the original precipitate consisting of nickel, cobalt, and iron, and from the weight thus obtained, calculate the percentage of nickel in the sample.

ELECTROLYTIC SEPARATION.

61. Determination of Copper.—Dissolve about .4 or .5 gram of the sample in dilute nitric acid, and evaporate to dryness on the water bath. Add 5 cubic centimeters of concentrate nitric acid to the residue, and dissolve it in 200 cubic centimeters of water. By means of the battery, deposit the copper from this solution on the negative electrode, following the directions given in Art. **20**, *Quantitative Analysis*, Part 1. When the copper is all deposited, hold the electrode over the beaker and wash the liquid adhering to it back into the solution by directing a fine stream of water from a wash bottle on to the electrode. Then wash in the usual manner, by dipping the electrode into several beakers of hot water, and finally into alcohol. Dry in an air bath at about 110°, cool in a desiccator, and weigh. From the weight of copper thus obtained, calculate the percentage of copper in the sample.

62. Determination of Nickel.—If a qualitative analysis has shown that the coin contains only copper and nickel, render the solution from which the copper has just been separated strongly alkaline with ammonia. heat it to 60° or 70°, and deposit the nickel by means of an electric current liberating about 10 cubic centimeters of electrolytic gas per minute. Ammonia will be expelled from the solution quite rapidly at this temperature, and as the solution must be kept distinctly alkaline all the time, small quantities of ammonia must be added frequently to take the place of that driven off by the heat. When the nickel is completely deposited, disconnect the apparatus; wash the electrode by dipping it into several beakers of hot water and then into alcohol, dry, cool, and weigh, and from the weight of nickel thus obtained, calculate the percentage of nickel in the sample.

If, in addition to copper and nickel, the coin contains iron and cobalt, the method must be modified as follows:

After separating the copper, heat the solution to boiling, and render it alkaline with ammonia. If iron is present, it will be precipitated as ferric hydrate. Filter, wash well with

hot water, wrap the precipitate in the filter, place in a crucible and ignite gently at first, but finally at the highest temperature of the blast lamp. Cool in a desiccator, weigh as ferric oxide Fe_2O_3, and from this weight, calculate the percentage of iron in the sample.

Render the filtrate strongly alkaline with ammonia, heat it to about 65°, and deposit the nickel and cobalt together on the negative electrode, by means of the electric current, in the same way that the nickel was deposited in the last instance. When the precipitation is complete, wash the electrode containing the two metals in the usual manner, by dipping it into hot water and alcohol, dry it in an air bath, cool in a desiccator, and weigh. The weight of nickel and cobalt is thus obtained.

Dissolve the metals from the electrode in a small quantity of nitric acid, and evaporate to a pasty condition on the water bath. Dissolve the residue in a few cubic centimeters of water, render the solution slightly alkaline with potassium hydrate, and add just enough acetic acid to completely dissolve the precipitate formed by the potassium hydrate. To this solution, add a strong solution of potassium nitrite that has been acidulated with acetic acid, stir well, and stand in a moderately warm place for 24 hours.

Filter, wash well with a 10-per-cent. solution of potassium acetate containing a little potassium nitrite. Dry the precipitate, remove it as completely as possible from the filter, and burn the latter. Add the precipitate to the filter ash, dissolve it in the least necessary quantity of hydrochloric acid, dilute to about 50 cubic centimeters, heat to boiling, precipitate the cobalt with a slight excess of sodium hydrate, and continue the boiling until the precipitate becomes black and of uniform texture. Filter, wash with hot water, ignite in a current of hydrogen, and weigh as metallic cobalt.

Instead of precipitating the cobalt as just described, it may be determined by electrolysis. To do this, dissolve the precipitate of potassium cobalt nitrite in the least necessary quantity of hydrochloric acid, evaporate nearly to dryness, add a few drops of concentrate nitric acid, and dissolve in

water. Render this solution distinctly alkaline with ammonia, heat it to 60° or 70°, and deposit the cobalt in the same way that the nickel was precipitated. Wash, dry, cool, and weigh the electrode containing the cobalt in the usual manner. From the weight of cobalt obtained by one of these methods, calculate the percentage of cobalt in the sample. Then subtract the weight of cobalt from the weight of nickel and cobalt previously obtained, and from the weight of nickel thus found, calculate the percentage of nickel in the sample.

GERMAN SILVER.

$$Cu + Zn + Ni$$

63. Determination of Copper.—The copper may be determined as sulphide by precipitating with hydrogen sulphide, or as metallic copper by depositing it electrolytically. As electrolytic methods are comparatively new, the first method is the most largely used at present.

1. Dissolve about 1 gram of the sample in the least necessary quantity of nitric acid, and evaporate to dryness on the water bath. Add 5 or 6 cubic centimeters of hydrochloric acid to the residue, dissolve it in 100 cubic centimeters of water, heat the solution to incipient boiling, and precipitate the copper as sulphide by leading a moderately rapid current of hydrogen sulphide through the solution, which should be in a covered beaker. Filter rapidly, wash without interruption with water containing hydrogen sulphide, and dry in an air bath. This precipitate invariably contains some zinc sulphide and must, consequently, be purified. Remove it as completely as possible from the filter, burn the latter, moisten the ash with nitric acid, and evaporate to dryness. Then add the precipitate, dissolve the whole in nitric acid and evaporate to dryness. Add about 5 cubic centimeters of concentrate hydrochloric acid, dissolve in 100 cubic centimeters of water, heat the solution to boiling, and again precipitate the copper with a current of hydrogen sulphide. The precipitate will now be free

from zinc. Filter, wash with water containing hydrogen sulphide, dry, ignite in a current of hydrogen with the addition of a little sulphur, and weigh as cuprous sulphide Cu_2S. From this weight, calculate the percentage of copper in the sample.

2. Dissolve about .5 gram of the sample in nitric acid and evaporate to dryness on the water bath. Add about 5 cubic centimeters of concentrate nitric acid to the residue, dissolve it in 200 cubic centimeters of water, and deposit the copper on the negative electrode, using an electric current that liberates from .5 to 1 cubic centimeter of electrolytic gas per minute. When all the copper is deposited, remove the electrodes from the solution, and while holding them over the beaker, wash the liquid adhering to them back into the solution. Then wash the electrode containing the copper by dipping it successively into three or four beakers of hot water and a beaker of alcohol. Dry the electrode and copper in an air bath at 110°, cool in a desiccator, and weigh. From the weight of copper thus obtained, calculate the percentage of copper in the sample.

64. Determination of Zinc.—If the copper was separated as sulphide, unite the two filtrates and boil until hydrogen sulphide is completely expelled, finally adding a few drops of nitric acid. In either case, evaporate the solution to about 150 cubic centimeters, add sodium carbonate drop by drop until the last drop produces a permanent precipitate, and dissolve this precipitate by adding a single drop of concentrate hydrochloric acid. When this solution is perfectly cold, conduct a current of hydrogen sulphide into it as long as a precipitate forms, then add a few drops of a dilute solution of sodium acetate, continue to lead hydrogen sulphide through the solution until it is thoroughly saturated, and allow it to stand for 12 hours in a moderately warm place. Filter off the zinc sulphide, wash at first with water containing a little ammonium nitrate and hydrogen sulphide, and then with water containing only a little hydrogen sulphide. If the above directions are carefully followed, the precipitate

will now be pure zinc sulphide and may be dried, ignited, and weighed, according to directions given later; but as a slight variation from the proper method of procedure may cause the precipitation of some nickel, it is best to dissolve the precipitate in the least necessary quantity of dilute nitric acid, evaporate the solution almost to dryness to expel most of the excess of acid, and then dilute to about 100 cubic centimeters. Render this solution almost neutral, by adding sodium carbonate until the last drop produces a precipitate, dissolve this with a drop of hydrochloric acid, and precipitate the zinc by a current of hydrogen sulphide in the same way that this was done in the first instance. After allowing the solution to stand for 12 hours for the precipitate to collect and settle, filter, and wash at first with water containing a little ammonium nitrate and hydrogen sulphide, and then with water containing only hydrogen sulphide. Dry the precipitate, remove it from the filter, burn the latter in a Rose crucible, add the precipitate together with a little sulphur, and ignite over a Bunsen burner in a current of hydrogen. Allow the precipitate to cool in a current of hydrogen, weigh as zinc sulphide ZnS, and from this weight, calculate the percentage of zinc in the sample.

65. Determination of Nickel.—Combine the two filtrates from the zinc sulphide, boil with the addition of a few drops of nitric acid, to expel all hydrogen sulphide, evaporate the solution to about 150 cubic centimeters, and determine the nickel by one of the following methods:

1. Render the solution strongly alkaline with ammonia, heat it to 65° or 70°, and deposit the nickel electrolytically by means of a current liberating from 5 to 12 cubic centimeters of electrolytic gas per minute. When the nickel is all deposited, wash the negative electrode containing the nickel, by dipping it into several beakers of hot water, and finally into a beaker of alcohol. Dry, cool, weigh, and from the weight of nickel thus obtained, calculate the percentage of nickel in the sample.

2. Wash the solution into a porcelain dish, heat it to

boiling, precipitate the nickel with an excess of sodium hydrate added in small successive portions while stirring constantly, and continue the boiling until the odor of ammonia has entirely disappeared. Then, to the gently boiling solution, add bromine water in small successive quantities, and with constant stirring, until the precipitate becomes black and of uniform texture, taking care that the solution remains alkaline throughout the operation. Allow the precipitate to settle, wash it 2 or 3 times by decantation with hot water, then filter, and wash on the filter with hot water, until the washings no longer have an alkaline reaction when tested with litmus paper. Dry the precipitate, remove it from the filter, burn the latter in a porcelain crucible, add a drop or two of concentrate nitric acid, and evaporate to dryness to change any nickel that may be reduced back to oxide. When cool, add the precipitate, ignite strongly, cool in a desiccator, weigh as nickel oxide NiO, and from this weight, calculate the percentage of nickel in the sample.

66. Separation of Zinc and Nickel from a Potassium-Cyanide Solution.—A method of separating zinc and nickel that is quite largely used at the present time, depends upon the deportment of their cyanides in a potassium-cyanide solution with potassium sulphide. The details of the method are as follows:

After evaporating the filtrate from the copper to 100 or 150 cubic centimeters, render it strongly alkaline with potassium hydrate, adding the reagent in the form of a concentrate solution. This will precipitate all of the nickel, and part of the zinc in the form of hydrates. Add a concentrate solution of potassium cyanide in sufficient quantity to dissolve the precipitate, but avoid any considerable excess. If the solution is very strongly alkaline, nearly neutralize it with hydrochloric acid, but still leave it distinctly alkaline. Then add a strong solution of potassium sulphide in sufficient quantity to precipitate all the zinc, but avoid a large excess of this reagent. Stir well with a glass rod, allow to stand for some time, filter, wash, dry, ignite, and weigh as zinc sulphide,

following the directions given in Art. **64.** From this weight, calculate the percentage of zinc in the sample.

Render the filtrate from the zinc sulphide slightly acid with hydrochloric acid, add 1 or 2 drops of concentrate nitric acid, and boil the solution until the odor of hydrocyanic acid can no longer be detected, showing that the cyanides have been broken up and the cyanogen expelled from the solution. Then proceed with the determination of nickel, using one of the methods described in Art. **65.**

ALLOY OF BISMUTH AND COPPER.

67. Determination of Bismuth.—Dissolve about .5 gram of the sample in a small quantity of dilute nitric acid, and evaporate to dryness on the water bath. Moisten the residue with a few drops of concentrate hydrochloric acid, mix it with a stirring rod, and then slowly add about 200 cubic centimeters of water, while stirring continuously. When the water has all been added, stir well, and stand aside until the white precipitate of bismuth oxychloride $BiOCl$ completely settles, leaving the supernatant liquid perfectly clear. Then add a little more water acidulated with hydrochloric acid, and observe if any further precipitation takes place. If it does, continue to add water until the bismuth is completely precipitated. If no precipitate is formed, the bismuth was all precipitated by the first addition of water. As soon as the bismuth is completely precipitated, and the precipitate has settled, filter on a weighed filter, wash with water containing a little hydrochloric acid, and dry in an air bath at 110°, until a constant weight is obtained. The increase in weight over the weight of the paper alone, is the weight of bismuth oxychloride $BiOCl$, which contains 80.20 per cent. of bismuth. From this, calculate the percentage of bismuth in the sample.

68. Determination of Copper.—Evaporate the filtrate from the bismuth oxychloride to about 150 cubic centimeters, heat it to boiling, and precipitate the copper as sulphide by leading a current of hydrogen sulphide through the gently

boiling solution. As soon as the precipitate settles, filter it rapidly, preferably with the aid of a filter pump, wash without interruption with water containing hydrogen sulphide, dry, ignite, with the addition of sulphur, in a current of hydrogen, and weigh as cuprous sulphide Cu_2S. From this weight, calculate the percentage of copper in the sample.

If preferred, the copper may be determined as oxide by following the directions given in Art. **16**, *Quantitative Analysis*, Part 1, or the filtrate from the bismuth may be evaporated to dryness with the addition of sulphuric acid, to expel the hydrochloric acid, the residue dissolved in about 150 cubic centimeters of water with the addition of 1 or 2 cubic centimeters of nitric acid, and the copper determined electrolytically as in the analysis of a silver coin (see Art. **40**).

ALLOY OF BISMUTH AND LEAD.

69. Determination of Bismuth.—Dissolve from .5 to .8 gram of the sample in nitric acid, and evaporate to a syrupy consistence on the water bath. Add a little water, stir the mixture well with a stirring rod, and again evaporate on the water bath. Repeat this four or five times to expel the nitric acid, then to the cold residue add a solution made by dissolving 1 gram of ammonium nitrate in 500 cubic centimeters of water, stir well, and stand aside for an hour or two for the precipitate of basic bismuth nitrate to collect and settle. Filter, and wash thoroughly with a solution of ammonium nitrate having the same strength as that used to precipitate the bismuth. Pure water cannot be used to wash this precipitate, for when it is used, the precipitate rapidly becomes more basic, and the washings, which have an acid reaction, contain bismuth. Dry the precipitate, remove it from the filter, cautiously burn the paper in a porcelain crucible, and, when cool, add a drop or two of nitric acid to the ash and evaporate to dryness. Add the precipitate to the residue in the crucible, and ignite it strongly over a Bunsen burner, while protecting the precipitate from the action

of reducing gases. Cool the precipitate in a desiccator, and weigh it as bismuth oxide Bi_2O_3, which contains 89.66 per cent. of bismuth. From this weight, calculate the percentage of bismuth in the sample.

As bismuth oxide is easily reduced, it is a good plan, after weighing as oxide, to ignite in a current of hydrogen, remove the flame, allowing the precipitate to cool in an atmosphere of hydrogen, and weigh as metallic bismuth as soon as the crucible becomes cool, thus checking the result obtained by weighing the bismuth as oxide.

70. Determination of Lead.—Evaporate the filtrate and washings from the bismuth to about 100 cubic centimeters, and precipitate the lead from this solution in the form of sulphate, by adding a slight excess of dilute sulphuric acid. Then add about 50 cubic centimeters of concentrate alcohol; stir well, and stand in a cool place for 4 hours for the precipitate to collect and settle. Filter through an asbestos felt in a porcelain Gooch crucible that has been dried and weighed. Wash the precipitate thoroughly with water containing about 1 per cent. of sulphuric acid, and then wash all the acid out of the precipitate and filter with half-strength alcohol. Dry the crucible and precipitate in an air bath heated to about 150°, until a constant weight is obtained, and from the resulting weight of lead sulphate, calculate the percentage of lead in the sample.

If preferred, the precipitate may be cautiously ignited over a Bunsen burner at a low temperature, cooled in a desiccator, and weighed; or, it may be filtered, washed, dried, and weighed according to one of the methods given in Arts. **26** and **27**, *Quantitative Analysis*, Part 1.

ALLOY OF ANTIMONY AND TIN.

71. Determination of Antimony.—Weigh about 1 gram of the finely divided sample into a porcelain dish, cover it with a watch glass, and oxidize the metals by the gradual

addition of concentrate nitric acid. When sufficient acid has been added, heat over a Bunsen burner until the residue appears perfectly white, and then evaporate to dryness on the water bath. Transfer the residue of oxides to a silver crucible, washing in the last particles adhering to the dish with a strong solution of sodium hydrate, and cautiously evaporate this solution to dryness. Mix the dry residue in the crucible with about eight times its bulk of solid sodium hydrate, and fuse it for about 15 minutes at a red heat over a Bunsen burner. The tin and antimony are thus changed into soluble sodium stannate and insoluble sodium metantimonate. When the crucible is moderately cool, place it in a porcelain dish, add hot water, and heat until the fusion is loosened from the crucible. Then remove the crucible from the porcelain dish, and wash it thoroughly by means of a wash bottle, allowing the washings to run back into the dish. The volume of the solution should now be about 200 cubic centimeters. Heat the contents of the dish over a Bunsen burner, and stir well with a glass rod until the fusion is thoroughly disintegrated; then remove it from the flame, allow it to stand a few moments, add one-third the volume of the solution of 90-per-cent. alcohol, stir well, and stand aside for the precipitate to settle. The tin will now all be in solution, while the antimony remains as an insoluble residue of sodium metantimonate. Filter, wash the precipitate two or three times with a solution consisting of 1 part of absolute alcohol to 2 parts of water, then wash clean with half-strength alcohol, and stand the filtrate aside to be treated later.

Remove as much as possible of the precipitate from the filter to a beaker. Then pour a solution consisting of equal parts of a saturated solution of tartaric acid and hydrochloric acid, on the filter, and receive the solution in a clean beaker. If this does not completely dissolve the precipitate remaining on the filter, pour the solution over it again, receiving it in a second clean beaker, and repeat this until the precipitate is completely dissolved. Pour this solution over the precipitate in the beaker, replace the beaker, which has just been

emptied, under the funnel, and wash the filter thoroughly with water. After the main precipitate has been dissolved, with the aid of gentle heat, if necessary, add the washings, and wash both of the beakers used to catch the acid solution into this solution, which will now contain all the antimony. The precipitate should be dissolved in the least necessary quantity of acid, as a large excess of hydrochloric acid prevents complete precipitation as sulphide. Dilute the solution containing antimony to about 250 cubic centimeters, place it on a water bath, and lead a current of hydrogen sulphide through it until the antimony is completely precipitated, and the solution is saturated with the gas. Then discontinue the hydrogen sulphide, and allow the solution to stand on the bath until the odor of hydrogen sulphide is barely perceptible. The expulsion of the excess of hydrogen sulphide may be hastened by leading a current of carbon dioxide through the solution while it is standing on the water bath. Filter rapidly, using a filter that has been previously dried at 110° and weighed, wash well with water containing a little hydrogen sulphide, dry at 110°, and weigh. The precipitate now consists of antimony sulphide, sulphur, and water, and a correction must be made. This is done by one, or both, of the methods described in Art. **60**, *Quantitative Analysis*, Part 1, and from the weight thus obtained, the percentage of antimony in the sample is calculated.

72. Determination of Tin.—Evaporate the alcoholic solution containing the tin to about 200 cubic centimeters, by heating it on the water bath, render the solution slightly but distinctly acid with hydrochloric acid, and precipitate the tin as sulphide by leading a current of hydrogen sulphide through the solution until it is thoroughly saturated. When the solution is acidified with hydrochloric acid, a white precipitate of sodium stannate frequently separates, but this has no significance, as it is readily converted into sulphide by hydrogen sulphide. After the solution is thoroughly saturated with hydrogen sulphide, let it stand for half an hour in a moderately warm place, then filter, and wash on

the filter with a solution of ammonium acetate containing a few drops of free acetic acid. Dry the precipitate in an air bath, transfer it to a watch glass, and burn the filter in a weighed porcelain crucible. When cool, moisten the ash with a few drops of nitric acid, evaporate, and ignite gently. After allowing the crucible to cool, add the precipitate, cover the crucible to avoid loss through decrepitation, and heat gently for several minutes. Then remove the cover, and continue to ignite gently until the sulphide is apparently all changed to oxide. Allow the crucible to cool, moisten the precipitate with a few drops of concentrate nitric acid, cover the crucible, ignite gently at first, then remove the cover and raise the temperature, finally heating at the highest temperature of the Bunsen burner. The sulphide will now be completely oxidized, but some sulphuric acid will remain in the precipitate. To expel this, allow the crucible and precipitate to cool, add a little dry ammonium carbonate, and ignite at a gradually increasing temperature, finally heating intensely. Repeat this treatment several times to be sure all sulphuric acid is expelled, then cool the crucible and precipitate in a desiccator, and weigh as stannic oxide SnO_2. From this weight, calculate the percentage of tin in the sample.

WOOD'S METAL.

$$Sn + Pb + Bi + Cd$$

73. Determination of Tin.—Weigh out about 1 gram of the finely divided sample, place it in a porcelain dish, add sufficient nitric acid of 1.3 Sp. Gr. to completely oxidize it, and evaporate to dryness on the water bath. Moisten the residue with about 1 cubic centimeter of nitric acid of the same strength as that used in dissolving the sample, add 100 cubic centimeters of water, and heat almost to boiling while stirring continuously. The tin, together with some of the lead and bismuth, will now be in the form of insoluble oxides, while the rest of the lead and bismuth, together with the cadmium, will be in solution in the form of nitrates. When

the precipitate has completely settled, filter, and wash with pure water until a test of the washings will scarcely color litmus paper. Dry the precipitate, remove it to a watch glass, burn the filter in a porcelain crucible, moisten the ash with a few drops of nitric acid, evaporate to dryness, and ignite gently. Then add the precipitate together with about five times its weight of a mixture of equal parts of sodium carbonate and sulphur, and fuse over a Bunsen burner. Allow the fusion to cool, and digest it with hot water until it is thoroughly disintegrated. The lead and bismuth will now be in the form of insoluble sulphides, while the tin will be dissolved in the form of sodium sulphostannate. After the precipitate has settled, filter, and wash the precipitate thoroughly with water containing a little hydrogen sulphide; then stand the precipitate in an air bath to dry and be treated later, and determine the tin in the filtrate as follows:

Slowly add hydrochloric acid to the solution while stirring constantly, until the reaction of the solution is distinctly acid, but avoid a large excess of acid. Then stand the solution on a water bath until the odor of hydrogen sulphide has nearly disappeared. Filter, and wash the precipitate thoroughly with a solution of ammonium acetate containing a few drops of free acetic acid. Dry the precipitate in an air bath, remove it from the filter, and burn the latter in a weighed porcelain crucible. Moisten the ash with a few drops of nitric acid, evaporate to dryness, and ignite gently; then add the precipitate, cover the crucible, and ignite gently for a few minutes with the cover on. When there is no longer any danger of loss through decrepitation, remove the cover and heat gently with free access of air so long as sulphur dioxide is given off. Then raise the temperature to the highest power of the Bunsen burner for a few minutes, and allow it to cool. Moisten the precipitate with a few drops of concentrate nitric acid, and cautiously ignite again, finally heating over the blast lamp. When the crucible and precipitate become moderately cool, add a little dry sodium carbonate and ignite strongly, raising the temperature gradually. Repeat this two or three times, finally igniting for a

few minutes at the full power of the blast lamp. The precipitate will now be pure stannic oxide SnO_2. Allow it to cool in a desiccator, weigh, and from this weight, calculate the percentage of tin in the sample.

74. Determination of Lead.—Remove the precipitate of lead and bismuth sulphides, set aside for further treatment, as completely as possible from the filter, and burn the paper in a porcelain crucible. Moisten the ash with nitric acid, evaporate to dryness on the water bath, add the precipitate, and dissolve the whole in half-strength nitric acid. Evaporate to dryness on the water bath, moisten the residue with 3 or 4 drops of nitric acid, dissolve it in the least necessary quantity of water, and wash this solution into the first filtrate containing the cadmium, together with most of the lead and bismuth. The solution will now contain all the lead, bismuth, and cadmium. Evaporate it to about 75 cubic centimeters, and precipitate the lead with a slight excess of sulphuric acid. Add about 30 cubic centimeters of absolute alcohol to the solution, stir well, and stand aside for at least 4 hours for the lead sulphate to completely separate. Filter through an asbestos felt in a porcelain Gooch crucible, wash at first with water containing 1 per cent. of sulphuric acid; then wash all the acid out with half-strength alcohol, dry at 150° in an air bath, cool in a desiccator, and weigh as lead sulphate $PbSO_4$. From this weight, calculate the percentage of lead in the sample.

If preferred, the lead sulphate may be filtered, dried, and weighed according to one of the methods described in Arts. **26** and **27**, *Quantitative Analysis*, Part 1, but in any case the precipitate should be washed first with water containing a little sulphuric acid, and then with half-strength alcohol, to remove all the acid.

This determination must be very carefully performed. The solution must contain sufficient nitric acid to hold the bismuth in solution, or part of it will be separated and weighed as lead; but a large excess of acid must be avoided, or the lead will not be completely precipitated. If

a precipitate separates from the solution before the sulphuric acid is added, just enough nitric acid must be added to redissolve it, but an excess must be avoided.

75. Determination of Bismuth.—Evaporate the filtrate from the lead sulphate to dryness on the water bath, add a little hydrochloric acid, and again evaporate to a syrupy consistence. Repeat the evaporation with hydrochloric acid once more in order to expel all nitric acid, and when the residue is nearly dry, add from 300 to 500 cubic centimeters of water, stir well, and stand aside for the precipitate to settle. This should completely precipitate the bismuth as oxychloride $BiOCl$, while the cadmium remains in solution. To learn if all the bismuth is precipitated, remove a little of the clear supernatant liquid to a watch glass and add a relatively large amount of water. If a precipitate results, more water must be added to the solution as long as a precipitate forms. If a precipitate is not produced on the watch glass, wash this solution back into the beaker and proceed with the determination. In either case, as soon as the precipitate settles, filter, wash with water that is slightly acidulated with hydrochloric acid, and stand the filtrate aside for the determination of cadmium. The precipitate of bismuth oxychloride will contain some sulphuric acid in this case, and consequently cannot be weighed directly. To obtain the precipitate in a pure form, dissolve it in the least necessary quantity of dilute nitric acid, and evaporate to a pasty consistence on a water bath. Add concentrate hydrochloric acid, and again evaporate almost to dryness. Repeat the addition of hydrochloric acid and evaporation, and, when almost dry, add a large quantity of water. Allow the precipitate to settle, filter through a weighed filter, wash the precipitate thoroughly with water that is slightly acidulated with hydrochloric acid, and dry in an air bath at 110°, until a constant weight is obtained. The precipitate is now bismuth oxychloride $BiOCl$, which contains 80.20 per cent. of bismuth, and from the weight of this, the percentage of bismuth in the sample is calculated.

76. Determination of Cadmium.—Evaporate the filtrate from the bismuth oxychloride, which contains the cadmium in solution, to about 150 cubic centimeters, and proceed to determine the cadmium, either as sulphide or oxide, by one of the following methods:

1. *Determination as Sulphide.*—Heat the solution gently over a water bath, and conduct a moderately rapid current of pure, washed hydrogen sulphide through it until the cadmium is completely precipitated, and the solution is thoroughly saturated with the gas. As soon as the precipitate settles, filter through a weighed filter, wash at first with hydrogen-sulphide water that has been slightly acidulated with hydrochloric acid, and then with pure water. Dry the precipitate in an air bath at 105° until a constant weight is obtained, and from the weight of cadmium sulphide thus found, calculate the percentage of cadmium in the sample. Cadmium sulphide CdS contains 77.78 per cent. of cadmium.

In order to prevent the possibility of sulphur being set free and weighed as cadmium sulphide, a strong solution of potassium cyanide is sometimes added in sufficient quantity to dissolve the precipitate at first formed, and the cadmium is then precipitated as sulphide by leading hydrogen sulphide through this solution. The subsequent treatment of the precipitate is the same as when potassium cyanide is not added.

2. *Determination as Oxide.*—Heat the solution nearly to boiling in a porcelain dish, and precipitate the cadmium as carbonate by adding sodium carbonate drop by drop, while stirring continuously, until the solution is distinctly alkaline. Boil for a few moments, allow the precipitate to settle, and decant the clear liquid through a filter. Add about 50 cubic centimeters of water, heat to boiling, allow the precipitate to settle, and decant the clear, supernatant fluid through the filter. Repeat this washing by decantation once, then bring the precipitate on to the filter, and wash thoroughly with hot water. Dry the precipitate in an air bath, remove it as completely as possible from the filter, saturate the latter with a concentrate solution of ammonium nitrate, and, after

drying, burn it cautiously in a weighed porcelain crucible. The ammonium nitrate supplies oxygen to burn the paper, and thus tends to prevent the reduction, and consequent volatilization, of the small amount of precipitate that invariably adheres to the filter. When the filter is completely burned, and the crucible has become cool, add the precipitate and ignite carefully, gradually increasing the temperature and finally heating strongly for about 10 minutes. Cool in a desiccator, and weigh. After weighing, again ignite strongly for 10 minutes, cool in a desiccator, and weigh. If the precipitate has lost weight during this second ignition, the operation must be repeated until the weight remains constant. This treatment is rendered necessary by the difficulty with which the last portions of carbon dioxide are expelled from the precipitate. When a constant weight is obtained, the precipitate is cadmium oxide CdO, which contains 87.50 per cent. of cadmium. From the weight thus obtained, calculate the percentage of cadmium in the sample.

77. Separation of Bismuth and Cadmium by Means of Sodium Carbonate and Potassium Cyanide.—Another method of separating bismuth and cadmium, which is probably more difficult to perform correctly than the one just described, depends upon the deportment of these metals with sodium carbonate and potassium cyanide. This method is quite largely used at present, and, consequently, it is best for the student to try it. The details are as follows:

After evaporating all alcohol from the filtrate from the lead sulphate, nearly neutralize the solution with sodium hydrate, heat nearly to boiling, slowly add sodium carbonate in sufficient quantity to completely precipitate the bismuth and cadmium, and then add a strong solution of potassium cyanide in sufficient quantity to completely dissolve the cadmium carbonate at first formed, leaving the bismuth precipitated. Heat the solution, in which the bismuth precipitate is suspended, on the water bath for half an hour. Then allow the precipitate to settle, filter, and wash with pure water. Dissolve the precipitate in the least necessary

quantity of dilute nitric acid, dilute the solution to about 150 cubic centimeters, heat it nearly to boiling, precipitate the bismuth as basic carbonate with a very slight excess of ammonium carbonate, and continue to heat nearly to boiling for some time. Allow the precipitate to settle, filter, and wash thoroughly with pure water. Dry the precipitate in an air bath, remove it to a watch glass, and cautiously burn the filter in a porcelain crucible. Add a few drops of nitric acid to the ash, evaporate to dryness, and ignite gently. Then, after the crucible has cooled, add the precipitate and ignite gently until the carbon dioxide is completely expelled and a constant weight is obtained. The precipitate is now bismuth oxide Bi_2O_3, which contains 89.66 per cent. of bismuth, and from the weight of this, the percentage of bismuth in the sample is calculated.

Heat the filtrate from the bismuth almost to boiling, and precipitate the cadmium as sulphide by slowly adding a slight excess of ammonium sulphide while stirring constantly. Allow the precipitate to settle, filter, and wash the precipitate thoroughly, using hydrogen-sulphide water at first and then pure water. Dissolve the precipitate in the least necessary quantity of half-strength nitric acid, and evaporate the solution nearly to dryness on the water bath. Add about 30 cubic centimeters of water to the residue, and stir well. If this does not produce a perfectly clear solution, it must be filtered, and the solid matter on the filter must be washed thoroughly with pure water. If the residue is completely dissolved, it is only necessary to dilute the solution. In either case, the clear solution should amount to about 100 cubic centimeters. Heat this solution almost to boiling, and precipitate the cadmium as carbonate by adding a solution of sodium carbonate, drop by drop, until the solution is distinctly alkaline, stirring the solution without interruption during the addition of the precipitant. Now heat the solution to boiling for a few moments, allow the precipitate to settle, filter, and proceed with the determination of cadmium as oxide, following the directions given in Art. **76**, 2.

The results obtained by this method are usually a trifle

low, and sometimes the latter part of the operation is omitted. In this case the precipitate obtained by ammonium sulphide is filtered on a weighed paper, washed thoroughly, dried at 105°, and weighed as cadmium sulphide. It is the writer's experience, however, that the results thus obtained are not as accurate as those obtained by following the directions just given, and weighing the cadmium as oxide.

BABBITT METAL.

$$Sn + Pb + Sb + Cu$$

78. Babbitt metal is an alloy of tin, lead, antimony, and copper largely used for bearings. Most of the so called "bearing" and "anti-friction" metals are composed of these same metals in varying proportions, and the same methods of analysis apply in all such cases. The separation of these metals is a rather difficult operation, and many methods of analysis have been proposed. Two very good methods are here given. They are both modifications of previously proposed methods, and either these methods, or slight modifications of them, are largely used. The student should make himself familiar with both methods, and then, if he wishes, he can work out modifications of them for himself.

FIRST METHOD.

79. Determination of Lead.—Weigh 1 gram of the finely divided alloy into a beaker having a capacity of about 250 cubic centimeters. Cover the sample with 4 or 5 grams of powdered tartaric acid, add 30 cubic centimeters of nitric acid having a specific gravity of 1.2, cover the beaker with a watch glass, and heat on the water bath until the sample is completely dissolved. Then, by means of a fine jet of water from the wash bottle, wash any particles of liquid that may have spattered against the watch glass back into the beaker, remove the watch glass, and evaporate the contents of the beaker to a pasty consistence. Add about 75 cubic

centimeters of hot water to this pasty residue, and stir it occasionally, while standing on the water bath, until the lead nitrate has completely dissolved. Part of the tin and antimony will be dissolved, and part will remain as a white powder. Now add a concentrate solution of potassium hydrate until the precipitate at first formed is almost completely dissolved in an excess of the reagent. The solution at this point will generally appear cloudy, as it would take a very large excess of the reagent to completely redissolve the copper hydrate formed. This cloudiness may be disregarded, as it has no influence on the analysis. Add 20 cubic centimeters of yellow sodium-sulphide solution,* cover the beaker, and digest 4 or 5 hours on the water bath, stirring from time to time. Allow the precipitate to settle, decant as much of the clear liquid as possible through a filter, and wash once by decantation with warm water, decanting as much of the liquid as possible without bringing any of the precipitate on to the filter. To the residue of sulphides, add 15 cubic centimeters of the yellow sodium-sulphide solution, cover the beaker, and again digest on the water bath for 2 hours. Then add 50 cubic centimeters of hot water, stir thoroughly, allow the precipitate to settle, filter through the same paper that was used in decanting the solution, and wash thoroughly and quickly on the filter, with water containing hydrogen sulphide. The precipitate is composed of the sulphides of lead and copper, and the antimony and tin are in the filtrate. Dry the precipitate, remove it as completely as possible to a small porcelain dish, place the filter in a porcelain crucible, and burn off the volatile matter, but do not attempt to burn off the carbon. Transfer the charred filter to the precipitate in the porcelain dish, moisten this with a few drops of concentrate nitric acid, cover the dish with a watch glass, add 10 cubic centimeters of fuming nitric acid, and digest on the

* To make this solution, dissolve 20 grams of sodium hydrate in 100 cubic centimeters of water, and when all is dissolved, lead a current of hydrogen sulphide into the solution until it is saturated. Pour this solution through a filter to remove any solid matter, and then stir in 100 milligrams of flowers of sulphur, which will dissolve, giving the solution a yellow color.

water bath until all sulphur has disappeared. Then add 10 cubic centimeters of one-third-strength sulphuric acid, and evaporate until all nitric acid is driven off. Add about 35 cubic centimeters of warm water, stir well, and stand aside until the precipitate has completely subsided. Filter, wash at first with water containing 1 per cent. of sulphuric acid, and then, after removing the filtrate, wash with half-strength alcohol until the sulphuric acid is washed out of the filter. As these alcoholic washings contain no metal, they may be thrown away. Dry the precipitate, remove it as completely as possible from the filter, and cautiously burn the latter in a porcelain crucible. When cool, add 3 drops of nitric acid and 1 or 2 drops of sulphuric acid to the ash, evaporate to dryness, and ignite very gently. Then add the precipitate, ignite gently over a Bunsen burner, cool in a desiccator, and weigh as lead sulphate $PbSO_4$. From this, calculate the percentage of lead in the sample.

If preferred, the precipitate may be collected in a porcelain Gooch crucible or on a weighed filter, dried at 110°, and weighed, but probably the method given is the one most frequently used. The porcelain Gooch crucible, however, is preferred by many chemists.

80. Determination of Copper.—Heat the filtrate from the lead sulphate to incipient boiling, and while holding it just at, or slightly below, the boiling point, lead in a rather rapid current of hydrogen sulphide until the copper is completely precipitated. As soon as the precipitate has settled, filter, and wash rapidly with water containing hydrogen sulphide. Dry the precipitate, remove it from the filter, and cautiously burn the latter in a Rose crucible. Add the precipitate, together with a little powdered sulphur, ignite in a current of hydrogen, as directed in Art. **18**, *Quantitative Analysis*, Part 1, cool in a desiccator, and weigh as cuprous sulphide Cu_2S. From this weight, calculate the percentage of copper in the sample.

As the filtrate from the lead sulphate contains the copper in the form of sulphate, together with a little free

sulphuric acid, the copper may readily be determined electrolytically, if preferred. All that is necessary in this case is to dilute the solution to about 150 cubic centimeters, and deposit the copper by means of the battery, as directed in Art. **20**, *Quantitative Analysis*, Part 1. It is best, however, to add a few drops of nitric acid before electrolyzing.

81. Determination of Antimony. — Dilute the filtrate from the mixed sulphides of lead and copper to about 300 cubic centimeters and slowly add hydrochloric acid, while stirring the solution, until it is distinctly acid, but avoid a large excess of acid. Then heat the solution on a water bath until only a faint odor of hydrogen sulphide remains. Allow the precipitate, which consists of the sulphides of tin and antimony, together with much free sulphur, to settle; decant the clear fluid through a filter, wash once by decantation, and then wash once or twice on the filter with pure water. Transfer as much as possible of the precipitate to a clean beaker, and dissolve the small amount of precipitate adhering to the filter in dilute sodium hydrate. Allow this solution to run through the filter into the beaker containing the precipitate, and wash the paper clean with pure water. The solution in the beaker should now amount to 75 or 80 cubic centimeters. To this, add from 20 to 25 grams of solid sodium hydrate, and stir until all is dissolved. If much heat is produced by the solution of the sodium hydrate, allow the solution to cool, then cautiously add 5 cubic centimeters of pure bromine, and digest on the water bath, keeping the beaker covered, until the sulphur is completely oxidized and the antimony is precipitated as white crystalline sodium metantimonate. Now remove a drop or two of the solution, and add to it an equal amount of concentrate hydrochloric acid. If this liberates bromine vapors, enough bromine has been added to the solution, but if bromine vapors are not given off, more bromine must be added and the solution must be heated a little longer on the water bath. Then boil the solution for a few minutes, allow it to cool,

add sufficient alcohol to make up from one-third to one-fourth of the total volume of the solution, stir well, and stand aside for at least 6 hours (longer, if necessary) for the precipitate to collect and settle. Filter, and wash with a mixture of 1 part of alcohol and 3 parts of water, to which a little sodium carbonate is added. The precipitate now contains the antimony as sodium metantimonate, generally mixed with a little free sulphur, and the filtrate contains the tin as sodium stannate. The latter is set aside to be treated for the separation of tin.

Transfer as much as possible of the precipitate to a beaker, and dissolve the small portion adhering to the filter in the least necessary quantity of a mixture of concentrate tartaric acid and half-strength hydrochloric acid, allowing the solution to run into the beaker containing the precipitate. If necessary, add more of this mixture of acids to completely dissolve the precipitate, then wash the filter, from which the precipitate was dissolved, with water, and receive the washings in the beaker with the rest of the antimony solution. If the solution contains any free sulphur, filter it off and wash well. The filtrate will now contain the antimony freed from elements that would interfere with its determination.

Dilute this solution to about 200 cubic centimeters, place it on the water bath, and when it has assumed the highest temperature that will be imparted to it by the bath, lead a rather rapid current of hydrogen sulphide through it until the antimony is completely precipitated. Let the beaker and contents stand on the water bath until only a faint odor of hydrogen sulphide is given off; then allow the precipitate to settle, filter, bringing the precipitate on a weighed filter, wash rapidly and well with water containing a little hydrogen sulphide, and then once or twice with pure water; dry at 110° and weigh.

This precipitate consists of antimony sulphide, sulphur, and water, and a correction must be made. To do this, remove as much of the precipitate as possible to a weighed porcelain boat—taking care not to get any of the paper—

and weigh boat and precipitate. Then place the boat and contents in a piece of combustion tubing, drawn out to a small opening at one end. Lead in dry carbon dioxide through a perforated stopper in the other end, and, when the air is expelled from the tube, bring a Bunsen burner under the boat, and heat carefully until no more sulphur vapors are given off, and the precipitate has assumed a metallic appearance. Allow the boat and precipitate to cool in the current of dry carbon dioxide and weigh as soon as cool. The precipitate is now pure antimony sulphide Sb_2S_3. From the weights thus obtained, calculate the weight of antimony sulphide in the original precipitate, and from this, calculate the percentage of antimony in the sample. Art. **60**, *Quantitative Analysis*, Part 1, should be read in connection with this determination.

82. Determination of Tin.—Dilute the filtrate from the antimony to about 250 cubic centimeters, render it distinctly acid with hydrochloric acid, and heat the solution until the bromine is all expelled. Then lead a current of hydrogen sulphide through the solution until the tin is completely precipitated and the solution is saturated with the gas. Let the beaker stand in a warm place until the precipitate settles, leaving the supernatant liquid clear. Filter, and wash the precipitate thoroughly with a solution of ammonium acetate containing a little free acetic acid. Dry the precipitate, remove it from the filter, and burn the latter in a porcelain crucible. Moisten the ash with a few drops of nitric acid and evaporate this to dryness. Then add the precipitate, cover the crucible, and ignite gently for a few minutes. Remove the cover and continue to ignite gently until the precipitate is apparently changed to oxide. Allow it to cool, add 3 or 4 drops of concentrate nitric acid, and ignite again, gently at first, with the crucible covered, but finally at the highest temperature of the Bunsen burner, with the cover removed. Let the crucible cool, add a little pure dry ammonium carbonate, and ignite again. Repeat this two or three times, finally igniting intensely. Allow the

crucible and precipitate to cool in a desiccator, weigh, and from the weight of stannic oxide SnO_2 thus obtained, calculate the percentage of tin in the sample.

SECOND METHOD.

83. Determination of Lead.—Weigh 1 gram of the finely divided alloy into a beaker, add 15 or 20 cubic centimeters of nitric acid of 1.2 Sp. Gr., cover the beaker, and heat on the water bath until the sample is completely decomposed. Then remove the watch glass, washing any liquid adhering to it back into the beaker, and evaporate to a pasty consistence on the water bath. Add from 8 to 10 cubic centimeters of water to this pasty residue, stir well, and then add a concentrate solution of sodium hydrate until the mixture is nearly, but not quite, neutral. Now add 20 cubic centimeters of freshly prepared yellow sodium-sulphide solution, cover the beaker, and heat to incipient boiling for half an hour. Add about 10 cubic centimeters of pure water, stir well, allow the precipitate to completely subside, and decant as much of the solution through a filter as possible without bringing any of the precipitate on the paper. To the precipitate add 15 cubic centimeters of yellow sodium sulphide, cover the beaker with a watch glass, heat the mixture over a Bunsen burner until it just begins to boil, then remove it to a water bath, and digest for an hour. Add about 20 cubic centimeters of water, stir well, and when the precipitate has settled, filter, using the paper through which the solution was decanted. Wash this precipitate thoroughly with water containing 1 per cent. of the sodium-sulphide solution used above. The precipitate now contains the lead and copper, while the antimony and tin are in the filtrate, which should be set aside and treated for these metals later.

Wash the precipitate into a beaker with the least necessary quantity of water, and add from one-third to one-half as much concentrate nitric acid as the total amount of water used in washing the precipitate from the paper. If any of

the precipitate remains on the paper, dissolve it in one-third-strength nitric acid, and let this solution run into the same beaker. Heat this mixture, while stirring it continuously, until the precipitate is completely dissolved, and filter out the free sulphur that separates. To the filtrate add about 12 cubic centimeters of a solution of sulphuric acid, made by adding 1 part of concentrate acid to 3 parts of water, and evaporate until the nitric acid is completely expelled. Add 35 or 40 cubic centimeters of water to the residue, stir well, and let the precipitate completely subside. Filter, and wash thoroughly with water containing 1 or 2 per cent. of sulphuric acid. Then remove the filtrate, which contains the copper, and wash the sulphuric acid out of the filter with half-strength alcohol, throwing these alcoholic washings away. Dry and weigh the precipitate as directed in Art. **79**, and from the weight of lead sulphate $PbSO_4$ thus obtained, calculate the percentage of lead in the sample.

84. Determination of Copper.—Dilute the filtrate from the lead sulphate to about 100 cubic centimeters, if the volume does not already amount to that much, heat the solution to boiling, and precipitate the copper by a rather rapid current of pure hydrogen sulphide. As soon as the precipitate settles, filter, and wash rapidly with water containing hydrogen sulphide. Dry the precipitate, ignite it with the addition of sulphur in a current of hydrogen, and weigh as cuprous sulphide Cu_2S, following the directions given in Art. **18**, *Quantitative Analysis*, Part 1. From the weight of cuprous sulphide thus obtained, calculate the percentage of copper in the sample. If preferred, a few drops of nitric acid may be added to the filtrate from the lead sulphate, the solution diluted to about 150 cubic centimeters, and the copper deposited electrolytically as described in Art. **20**, *Quantitative Analysis*, Part 1. Some chemists prefer to precipitate the copper as sulphide, dissolve the precipitate in dilute nitric acid, boil the filtrate to expel hydrogen sulphide, evaporate it to about 5 cubic centimeters, dilute to about 150 cubic centimeters, and deposit the copper electrolytically.

85. Determination of Antimony.—If the filtrate from the sulphides of lead and copper does not amount to about 75 cubic centimeters, dilute it to this volume, boil, and cautiously add fine crystals of pure oxalic acid until the sodium sulphide is completely decomposed and the solution contains a milky separation of free sulphur, mixed with a precipitate which usually appears black at first. Enough oxalic acid must always be added. A moderate excess does no harm. Boil this solution for half an hour, and then while hot, pass a rather rapid current of hydrogen sulphide through it for 15 minutes. This will precipitate the antimony as sulphide, and the tin will remain in solution. As soon as the precipitate has settled, filter, using a filter that has been dried at 110°, and weighed, and wash at first with warm water containing hydrogen sulphide and then once or twice with pure hot water. Dry the precipitate on the filter at 110° in an air bath, and weigh. The precipitate consists of antimony sulphide, sulphur, and water, and a correction must be made as directed in Art. **81.** From the weights thus obtained, calculate the percentage of antimony in the sample

86. Determination of Tin.—To the filtrate from the antimony sulphide, add 10 cubic centimeters of concentrate sulphuric acid, and evaporate over a Bunsen burner until white fumes of sulphur trioxide begin to be given off. Allow the residue to cool, cautiously add 75 cubic centimeters of water, stir well, and filter quickly. Wash the filter until the filtrate and washings amount to about 125 cubic centimeters. Place this solution on the water bath, and pass a rather rapid current of hydrogen sulphide through it until the tin is completely precipitated, and the solution is saturated with the gas. Cover the beaker with a watch glass and let it stand on the water bath for half an hour. Then filter, and wash the precipitate thoroughly with a solution of ammonium acetate containing a little free acetic acid. Dry the precipitate, remove it from the filter, and burn the latter in a weighed porcelain crucible. After moistening the ash with

a few drops of concentrate nitric acid and evaporating to dryness, add the precipitate, ignite gently with the cover on at first, and afterwards with the cover removed. Moisten the cool precipitate with a few drops of concentrate nitric acid, ignite gently at first, with the cover on, and when dry, remove the cover and heat strongly. Then ignite several times with the addition of small quantities of dry ammonium carbonate, finally heating intensely. Cool in a desiccator, and weigh as stannic oxide SnO_2. From this weight, calculate the percentage of tin in the sample.

ANALYSIS OF MINERALS.

LIMESTONE.

87. Limestone is essentially calcium carbonate, but as it occurs in nature it always contains other substances. The constituents usually determined are insoluble matter (silica), oxides of iron, aluminum, calcium, and magnesium; but, in addition to these substances, the limestone always contains minute quantities of other elements, and when the stone is to be used for certain purposes the determination of phosphorus and sulphur becomes important. For the determination of the constituents usually sought, only one sample is used; but, when phosphorus and sulphur are estimated, a separate portion of the original sample is taken for each of these determinations.

As a rule the calcium and magnesium are weighed as oxide and pyrophosphate, respectively, and from these weights the corresponding amounts of the carbonates are calculated, but sometimes the calcium and magnesium are reported as oxides, and the carbon dioxide is determined in a separate portion of the sample. Although the latter method does not give so complete an idea of the composition of the stone to a person not familiar with chemistry, it is the more logical of the two, as by this method the chemist reports exactly what he finds rather than what he surmises.

CONSTITUENTS USUALLY DETERMINED.

88. Determination of Silica.—Weigh 1 gram of the finely ground sample, which has been dried at about 125° in an air bath, into a porcelain dish, and add 25 cubic centimeters of water. Cover the dish with a watch glass, add slowly 15 cubic centimeters of concentrate hydrochloric acid, and warm on a water bath until effervescence has ceased. Then remove the watch glass, wash any liquid that has spattered on it back into the dish, add 5 or 6 drops of concentrate nitric acid to the solution, and evaporate to dryness. Remove the dish to a gauze or piece of sheet iron over a Bunsen burner, and heat gently until the odor of hydrochloric acid can no longer be detected and the calcium chloride just begins to fuse, but avoid excessive ignition, as this may render the oxides of iron and aluminum insoluble in hydrochloric acid, and cause the silica to partially reunite with bases. To this residue, add 6 or 8 cubic centimeters of concentrate hydrochloric acid, and warm gently till the iron salts are dissolved; then add 50 cubic centimeters of water, and heat the solution, while stirring it continuously, until it begins to boil. Allow the solution to stand a few minutes for the precipitate to settle, filter through a small ashless filter, and wash thoroughly. Fold the filter carefully around the precipitate, place them in a platinum crucible, ignite cautiously at first to burn off the paper, and afterward ignite strongly over the blast lamp. Cool in a desiccator, and weigh as "insoluble silicious matter."

If this precipitate is perfectly white, and is small in quantity, it consists entirely of silica SiO_2, and for ordinary purposes may be reported as such; but if the silicious residue is large, or is more or less colored, it contains other substances and must be treated further. The treatment necessary will depend largely upon the amount and color of the residue, and the purpose of the analysis. If the residue is only of moderate quantity, and is white, or only slightly colored, it will contain very little, if any, material, except iron and alumina, in addition to the silica, and the first method will be

sufficiently accurate. In fact, this method is sufficiently accurate for technical purposes in nearly every case. But if the residue is very large or darkly colored, other constituents may be present, and the second method is the better in this case. Probably the second method is the more accurate of the two, and should be employed whenever strict accuracy is required.

1. Moisten the precipitate of insoluble silicious matter with 3 or 4 drops of pure water, cover it with hydrofluoric acid, add a few drops of sulphuric acid, evaporate to dryness, and cautiously ignite at a gradually increasing temperature, finally heating intensely to drive off all sulphuric acid. Cool in a desiccator, and weigh. The loss in weight is the weight of silica, which is dissolved by the hydrofluoric acid and volatilized. From this, the percentage of silica SiO_2 is calculated. To the residue in the crucible, which consists almost entirely of the oxides of iron and aluminum, add 4 or 5 cubic centimeters of pure, concentrate hydrochloric acid, and heat until this is evaporated to about 1 cubic centimeter, then add 2 or 3 cubic centimeters of water, heat to boiling, and wash the contents of the crucible into the filtrate from the insoluble silicious matter. If any of the iron and alumina remain undissolved, this does not matter greatly, as they are to be separated from this solution next.

2. Mix the insoluble silicious matter in the platinum crucible with 8 or 10 times its weight of a mixture of equal parts of dry sodium and potassium carbonates, heat over a Bunsen burner until the mass begins to cake together, and then over a blast lamp, until the mass is in a state of quiet fusion. Remove the crucible containing the fusion from the flame, and while holding it in a slanting position, slowly rotate it so that the fusion will solidify well up on the sides of the crucible, and thus expose a greater surface to the action of solvents. When cool, place the crucible in a porcelain dish, add hot water, a little at a time, and apply heat until the fusion dissolves. If the fusion dissolves very slowly, hydrochloric acid may be added towards the end of the process, but it should not be added at first, as it tends to

form a gelatinous precipitate over the surface of the fusion and thus impedes, rather than hastens, solution. Either during solution, or after solution is complete, render the liquid distinctly acid with hydrochloric acid, taking care to avoid loss by spattering during effervescence, and evaporate to dryness on the water bath. Transfer the dish to a wire gauze or sheet-iron plate, and heat over a Bunsen burner at about 150°, until the hydrochloric acid is driven off, but avoid a much higher temperature. After allowing the residue to cool, add 5 cubic centimeters of concentrate hydrochloric acid, heat gently for a few minutes, then add 20 cubic centimeters of water, heat to boiling, and finally dilute to 50 cubic centimeters. Filter, wash thoroughly with hot water, and ignite in a platinum crucible in the same way that the insoluble silicious matter was ignited. Cool in a desiccator, and weigh as silica SiO_2.

The filtrate will contain iron, aluminum, calcium, and magnesium, if these were present in the silicious residue, and is to be treated in the same manner as the filtrate from the silicious matter, and the results obtained are added to the percentages found in the main solution. The two solutions are sometimes united and the analysis completed in one operation, but it is best to analyze them separately and add the results, as when united, the large amount of calcium in the main solution will invariably carry down some of the sodium and potassium salts introduced with the filtrate from the fusion, and cause much trouble, if not the loss of the analysis. The calcium and magnesium found in this portion should be reported as oxides at all events.

89. Determination of Iron and Alumina.—Heat the filtrate from the insoluble silicious matter to boiling, and slowly add ammonia, while stirring continuously, until a very slight excess has been added. If the precipitate formed is rather large and light colored, dissolve it in 1 or 2 cubic centimeters of concentrate hydrochloric acid, and reprecipitate with a very slight excess of ammonia, in order to introduce enough ammonium chloride into the liquid to hold

everything except iron and aluminum in solution. In either case, boil the solution for a few moments after all the ammonia is added, and be sure that the solution remains alkaline, but any considerable excess of ammonia must be avoided. As soon as the precipitate settles, filter, and wash thoroughly with hot water. Fold the filter around the precipitate, place them together in a platinum crucible, and ignite, gently at first, to burn off the paper, but finally at the full power of a blast lamp. Cool in a desiccator, and weigh as oxides of iron and aluminum, Fe_2O_3 and Al_2O_3. As a rule, the percentage of the two oxides is all that is required, but occasionally the percentage of each oxide is wanted. When this happens, they should be separated as directed in Art. **95.**

90. Determination of Calcium Oxide or Carbonate.—If the filtrate from the iron and alumina greatly exceeds 200 cubic centimeters in volume, evaporate it to about this bulk, and to the boiling solution add 5 cubic centimeters of concentrate ammonia, then add about 35 cubic centimeters of a saturated solution of ammonium oxalate, and continue the boiling for a few moments. Enough ammonium oxalate must be added to convert all the calcium and magnesium into oxalates or the precipitation of calcium will not be complete. Stand the beaker and contents in a moderately warm place for at least 4 hours, for the precipitate to collect and settle. In the analysis of limestone for technical purposes, the solution is sometimes only allowed to stand for 15 or 20 minutes, and satisfactory results are thus obtained, but if exact results are sought, it should be allowed to stand at least 4 hours, for the last traces of calcium are only precipitated after standing for some time. Filter, and wash thoroughly with hot water containing 1 or 2 per cent. of ammonia, dry in an air bath, remove the precipitate from the filter, and burn the latter in a weighed platinum crucible. When cool, add the precipitate, heat gently for a few moments, then increase the temperature, and ignite at the full power of the blast lamp for 10 or

15 minutes. Let the precipitate cool, add 2 or 3 drops of water, and again ignite at the full power of the blast lamp for 10 minutes, after heating gently at first to expel the water. Cool in a desiccator, and weigh as soon as cool. Ignite the precipitate again for 10 minutes, cool in a desiccator, and weigh as soon as cool. If this weight is lower than the first one, the ignition must be repeated until a constant weight is obtained. The precipitate is now calcium oxide CaO, and if it is to be reported as such, no calculation is necessary. If, however, the ordinary method of reporting results is to be followed, the weight of calcium carbonate is obtained by multiplying the weight of calcium oxide by 1.7857.

If preferred, the precipitate of calcium oxalate may be converted into sulphate and weighed as such, by following the directions given in Art. **40,** *Quantitative Analysis*, Part 1, or the precipitate may be washed with pure hot water, and the calcium oxide (lime) determined volumetrically as directed in Art. **100,** *Quantitative Analysis*, Part 1.

91. Determination of Magnesium Oxide or Carbonate.—Evaporate the filtrate from the calcium oxalate to about 250 cubic centimeters, and add about 25 cubic centimeters of a saturated solution of microcosmic salt $HNaNH_4PO_4$, while stirring continuously. Then cool the solution by standing the beaker containing it in ice water, and add about 50 cubic centimeters of concentrate ammonia, adding the first portion drop by drop while stirring continuously. After the ammonia is all added, stir several times while the precipitate is forming, but in all the stirring take care not to strike the sides or bottom of the beaker with the rod; then cover the beaker with a watch glass and stand it aside for at least 6 hours; or, better still, allow it to stand overnight. Filter, and wash the precipitate thoroughly with a solution made by mixing 150 cubic centimeters of concentrate ammonia with 350 cubic centimeters of water, and adding 50 grams of ammonium nitrate. Dry the precipitate in an air bath, remove it from the filter, and burn the

latter in a porcelain crucible. When cool, add the precipitate, and ignite intensely over the blast lamp for 10 or 15 minutes. Cool in a desiccator and weigh as magnesium pyrophosphate $Mg_2P_2O_7$, which, multiplied by .36036, gives the weight of magnesium oxide MgO; or, multiplied by .75676, gives the weight of magnesium carbonate $MgCO_3$.

CONSTITUENTS SOMETIMES REQUIRED.

92. Determination of Carbon Dioxide.—If the calcium and magnesium in the limestone are calculated to carbonates, a determination of carbon dioxide is not required, but if they are reported as oxides, the carbon dioxide should be determined and its percentage reported. The following simple and rapid method yields satisfactory results if carefully performed. In fact, it is the writer's experience that after a little practice, very accurate results may be obtained by this method.

Place about 4.5 grams of borax glass in a weighed platinum crucible, heat moderately until it is in a state of quiet fusion, cool in a desiccator, and weigh. As the weight of the crucible is known, the weight of perfectly dry borax is thus obtained. If it is somewhat more than 4 grams, sufficient borax has been taken, otherwise add more and fuse again. After exactly balancing the crucible containing the borax, leave it standing on the pan of the balance; add a 1-gram weight to the weights on the other pan, and then add just enough of the powdered sample to again exactly balance it; 1 gram of the sample will thus be weighed off. Now transfer the crucible to a tripod, apply heat, gradually increasing the temperature until the crucible is heated to redness, and maintain this temperature until the contents are in a state of quiet fusion. A few bubbles of gas will always remain in the fusion, but these have no influence on the result. Cool the crucible and contents in a desiccator, and weigh. The loss in weight is the weight of carbon dioxide.

If carefully performed, this method yields very satisfactory

results, and it is commended by its simplicity, but care is necessary. If strongly ignited, the borax rapidly suffers loss, so a red heat is all that is safe to apply.

There is always a chance that other substances may be present that would be volatilized, and consequently be determined as carbon dioxide, when this method is used; hence, when absolute accuracy is required, the carbon dioxide is usually evolved by treating the sample with acid, absorbed in soda lime, and weighed directly as described in Art. **21**, 1.

93. Determination of Phosphorus.—Weigh 5 grams of the pulverized sample into a porcelain dish, add about 40 cubic centimeters of water, cover the dish, and then cautiously add 20 cubic centimeters of concentrate hydrochloric acid. As soon as the action slackens, place on a water bath, and when effervescence ceases, remove the cover and evaporate to dryness. Heat the dish very gently over a Bunsen burner, or place it in an air bath, heated to about 115°, for an hour, to render the silica anhydrous. Add 15 cubic centimeters of concentrate nitric acid to the residue, heat gently, then add 60 cubic centimeters of water, and heat to boiling. Filter, and wash with 60 or 70 cubic centimeters of hot water, receiving the filtrate and washings in a flask having a capacity of 500 or 600 cubic centimeters. Add nearly enough concentrate ammonia to neutralize the nitric acid, but leave the solution distinctly acid. Heat the solution to exactly 85°, add 50 cubic centimeters of ammonium molybdate solution, stopper the flask, and shake for 5 minutes. Then stand the flask in a moderately warm place for from 4 to 6 hours. The solution should keep a temperature of about 40°, but not above 50°. Filter, and wash the precipitate on the filter six times with water containing 2 per cent. of nitric acid.

When the washings have all run through, throw them away and place the flask in which precipitation was made under the funnel. Pour 2 or 3 cubic centimeters of concentrate ammonia on the precipitate, and immediately stir it

up by directing a fine stream of hot water from a wash bottle upon it. When water amounting to about three times the volume of the ammonia has been added in this way, allow the solution to run through into the flask. Now remove the flask, put a small beaker in its place under the funnel, run the solution around the sides of the flask to dissolve any "yellow precipitate" that may adhere to the glass, and then pour it back on to the filter and allow it to run through again. The precipitate should now be all dissolved. Add a few drops of ammonia to the filter, then pour a few cubic centimeters of water into the flask, rinse it around and pour this on the filter. Wash the flask out once more in this way, pouring the washings on the filter, and then wash the filter twice with hot water. The phosphorus will now be all in the filtrate, which should have a volume of from 30 to 50 cubic centimeters. Nearly neutralize this solution with hydrochloric acid, but leave it distinctly alkaline. Cool it by standing the beaker in ice water, and when quite cold, slowly add 10 cubic centimeters of magnesia mixture* while stirring the solution continuously. After the reagent has all been added, add one-third the volume of the solution of concentrate ammonia, and stand in a cold place for 4 or 6 hours for the precipitate to collect and settle. Filter, and wash the precipitate with a mixture of 1 part of ammonia and 3 parts of water, to each 100 cubic centimeters of which are added 3 or 4 grams of solid ammonium nitrate. Dry the precipitate in an air bath, remove it as completely as possible from the filter, and burn the latter in a weighed porcelain crucible. Add the precipitate, ignite 10 minutes at the highest power of the blast lamp, cool in a desiccator, and weigh as magnesium pyrophosphate $Mg_2P_2O_7$, which contains 27.93 per cent. of phosphorus, or 63.96 per cent. of phosphoric anhydride P_2O_5.

As a rule, all phosphates should be ignited in a porcelain crucible, as the phosphorus is likely to attack platinum, especially if reducing agents are present, and it is best to

* Directions for making magnesia mixture are given in the foot note to Art. 58, *Quantitative Analysis*, Part 1.

always follow this rule. If care is taken, however, and the precipitate is all removed from the filter, an experienced chemist may ignite this precipitate in a platinum crucible without injuring it, and this is usually done in commercial laboratories.

94. Determination of Sulphur.—Weigh 5 grams of the dry pulverized sample into a porcelain dish, cover with a watch glass, and dissolve the sample in a mixture of 15 cubic centimeters of concentrate hydrochloric acid, 5 cubic centimeters of concentrate nitric acid, and 10 cubic centimeters of water. As soon as the violent action is over, heat to boiling, and when effervescence entirely ceases, remove the cover, wash anything adhering to it into the solution, add 10 cubic centimeters of concentrate hydrochloric acid, and evaporate to dryness to expel all nitric acid, and render the silica insoluble. Moisten the residue with 1 cubic centimeter of concentrate hydrochloric acid, add 50 cubic centimeters of water, heat just to boiling, filter off any insoluble matter, and wash the precipitate with 50 or 60 cubic centimeters of hot water. Add 5 cubic centimeters of ammonium chloride to the filtrate, heat it to boiling, and precipitate the sulphur as barium sulphate, by adding 5 cubic centimeters of barium-chloride solution while stirring constantly. As soon as the reagent is all added, remove the solution to a warm place, and allow it to stand for at least 4 hours for the precipitate to collect and settle. Decant the clear liquid through the asbestos felt of a Gooch crucible that has been ignited and weighed. Add hot water to the precipitate, bring it to boiling, allow the precipitate to settle, filter through the Gooch crucible, and wash thoroughly on the felt with hot water, finally sucking as much water as possible out of the felt by means of the filter pump. Heat the crucible over a Bunsen burner, gently at first to drive off moisture, and then increase the temperature to dull redness for 5 minutes. Cool in a desiccator, and weigh as barium sulphate $BaSO_4$, which contains 13.73 per cent. of sulphur.

If preferred, the precipitate may be collected on a filter instead of a Gooch felt. In this case, filter, and wash in the manner just described, except that a filter paper is used instead of a Gooch crucible. Dry the precipitate in an air bath, remove it as completely as possible from the filter, and cautiously burn the latter in a weighed porcelain crucible. Moisten the ash with 2 or 3 drops of concentrate nitric acid and a drop of concentrate sulphuric acid, evaporate to dryness, and ignite to drive off all sulphuric acid. When the crucible is cool, add the precipitate, heat to dull redness for 5 minutes, cool in a desiccator, and weigh as barium sulphate $BaSO_4$.

As this precipitate is quite easily decomposed by heat, and is readily reduced, the writer prefers the use of a Gooch crucible. If a filter is used, the particles adhering to it are reduced, and sulphuric acid must be added; and when this is driven off, if not carefully done, the precipitate will again be broken up by the heat. With proper care, however, accurate results may be obtained by this method.

95. Separation of Iron and Alumina.—As a rule, all that is required is a determination of the oxides of iron and aluminum together; but occasionally, the percentage of each of these oxides is required. When this is the case, after determining the oxides together, the oxide of iron is determined separately, and this, subtracted from the combined oxides, gives the amount of alumina. Of the several methods proposed and used for this purpose, the writer prefers the following:

After determining the iron and alumina together, weigh out a fresh sample of the pulverized stone, amounting to 1 gram; place it in a porcelain dish, cover it with 25 cubic centimeters of water, slowly add 15 cubic centimeters of concentrate hydrochloric acid, and when effervescence ceases, evaporate to dryness, after adding 5 or 6 drops of concentrate nitric acid. Add from 5 to 8 cubic centimeters of concentrate hydrochloric acid to the residue, heat gently,

and mix it with a stirring rod for a few moments; then add 50 cubic centimeters of water, and heat to boiling; filter off the insoluble matter, and wash thoroughly with hot water. Heat the filtrate to boiling and precipitate the iron and alumina with a slight excess of ammonia, as in the regular analysis. As soon as the precipitate settles, filter, and wash once or twice with hot water. Dissolve the damp precipitate with the least necessary quantity of hot dilute hydrochloric acid, receiving the solution in a flask. If the precipitate is small, it is best to dissolve it all on the filter and allow the solution to run through the paper. If a few cubic centimeters of the acid do not dissolve the precipitate, pour the solution back on the paper and let it run through again; and repeat this until the precipitate is dissolved; or, if necessary, add a little fresh acid. When all is dissolved, wash the filter with water and a few more drops of hydrochloric acid, allowing the washings to run into the flask with the main solution. The solution should not amount to more than about 100 cubic centimeters. To it, add a little more granulated zinc than will be required to unite with all the free acid present—10 grams will usually be sufficient—place a small funnel in the neck of the flask, and heat it moderately, until the action is quite violent. Continue to heat gently until the acid is almost completely neutralized, but stop before basic iron salts begin to separate. Add 15 cubic centimeters of one-third-strength sulphuric acid to this solution, and after it has acted on the remaining zinc for a few moments, pour the solution, together with the zinc still undissolved, on a large folded filter, receiving the filtrate in a rather large beaker or porcelain dish. Wash the filter once by filling it with cold water and allowing it to run through, then dilute the solution to 400 or 500 cubic centimeters with cold water, and titrate at once with a standard solution of potassium permanganate. The solution must be quite cool when titrated, and, if very warm, the flask containing it should be placed in ice water before the sulphuric acid is added. If not very warm, the cold water added in washing and diluting will cool it sufficiently.

As zinc always contains a small amount of matter that will reduce permanganate, and exact results are required in this case, a correction must be made. This is done as follows:

Place a mixture of hydrochloric acid and water, having about the same volume as the solution of iron and alumina, and containing about the same amount of free acid, in a flask. Add to this exactly the same weight of zinc that was used in reducing the iron, place a small funnel in the neck of the flask, and heat it as in the case of the iron and alumina. When the hydrochloric acid is nearly neutralized, add sulphuric acid, filter, wash, dilute, and titrate with permanganate, treating this blank as nearly as possible in the same way that the solution of iron and alumina was treated. The volume of permanganate used by the blank, subtracted from the amount used in titrating the solution of iron and aluminum, gives the volume used in oxidizing the iron, and from this, the weight of iron in the sample is calculated. The weight of iron oxide Fe_2O_3 is readily calculated from the weight of iron, and this weight, subtracted from the weight of the combined oxides, gives the weight of alumina Al_2O_3.

ZINC BLENDE.

96. Zinc blende is essentially the sulphide of zinc, but it always contains more or less impurity. The foreign matter clinging to the outside of the sample—known as gangue—may consist of silica alone, or may be a silicious mixture. In addition to silica, zinc blende frequently contains small quantities of lead, cadmium, copper, iron, and manganese as impurities. The method to be employed in analyzing zinc blende depends largely upon the purpose of the analysis and the composition of the sample, and a careful qualitative examination should be made before the quantitative analysis is commenced. If only silica and zinc sulphide are present, the analysis is short and simple, while the presence of each of the impurities lengthens and complicates it.

WHEN SILICA IS THE ONLY IMPURITY.

97. Determination of Silica.—Grind somewhat more than a gram of the substance to a fine powder, dry it in an air bath heated to 100° for an hour, and allow it to cool in a desiccator. Weigh 1 gram of this dry sample into a beaker or porcelain dish, cover it with a watch glass, and add fuming nitric acid drop by drop. After the acid has acted for some time in the cold, heat on the water bath until red fumes are no longer given off, then remove the watch glass, wash any particles that may have spattered on to it back into the dish with the least necessary quantity of water, and evaporate to dryness. Moisten the residue with concentrate hydrochloric acid, and again evaporate to dryness on the water bath. Add about 2 cubic centimeters of concentrate hydrochloric acid to the residue, pour on about 100 cubic centimeters of hot water, and boil for a few minutes over a Bunsen burner, to dissolve all of the zinc. Allow the insoluble matter to settle, filter, and wash well on the paper with hot water. Wrap the filter around the precipitate, place it in a platinum crucible, and ignite gently at first to expel the moisture and burn the paper, but finally ignite intensely over the blast lamp for a few minutes. Cool in a desiccator, and weigh as silica SiO_2.

98. Determination of Zinc.—Heat the filtrate from the silica to boiling in a porcelain dish, and to this gently boiling solution, add sodium carbonate, drop by drop, while stirring continuously, until the reaction of the liquid is distinctly alkaline. Continue the boiling for 5 or 10 minutes, allow the precipitate to completely subside, and pour the clear liquid through a filter. Add 50 or 60 cubic centimeters of hot water to the precipitate, heat it to boiling, allow the precipitate to settle, filter, using the paper through which the clear liquid was poured, and wash thoroughly with hot water. Dry the precipitate, remove it as completely as possible from the filter, and cautiously burn the latter in a porcelain crucible. When cool, add the precipitate and ignite gently at first, but gradually increasing the temperature to the

highest power of the Bunsen burner, or ignite moderately over a blast lamp. Cool in a desiccator, and weigh as zinc oxide ZnO, which contains 80.26 per cent. of zinc.

It may be mentioned at this point, that if iron is the only impurity besides the silica, this method may be employed, and the iron, which will be precipitated with the zinc, may be determined in this precipitate. If this is done, dissolve the precipitate containing the oxides of zinc and iron by digesting it on a water bath with concentrate hydrochloric acid. Reduce the iron in this solution with stannous chloride, and titrate with standard potassium bichromate, following the directions given in Art. **99**, *Quantitative Analysis*, Part I. From the weight of iron thus obtained, calculate the weight of ferric oxide, and subtract this weight from the weight of the mixed oxides, before calculating the percentage of zinc.

99. Determination of Sulphur.—Evaporate the filtrate and washings from the zinc precipitate to about 200 cubic centimeters after rendering slightly acid with hydrochloric acid, and to this gently boiling solution add a slight excess of barium-chloride solution, while stirring continuously. Continue the boiling for a few moments after all the reagent has been added, and then stand on a water bath, or some equally warm place, for 4 or 5 hours for the precipitate to settle and become more dense. Filter, and wash thoroughly on the filter with hot water. Dry the precipitate in an air bath, remove it as completely as possible from the filter, and burn the latter in a porcelain crucible. When cool, moisten the ash with a drop of concentrate sulphuric acid, and heat, gently at first, but gradually increase the temperature to dull redness to expel the excess of acid. After allowing the crucible to cool, add the precipitate and again ignite, gradually increasing the heat until the crucible assumes a dull-red color, and hold it at this temperature for 10 minutes. Allow the crucible and precipitate to cool in a desiccator, and weigh as barium sulphate $BaSO_4$, which contains 13.73 per cent. of sulphur. From this, calculate the percentage of sulphur in the sample.

WHEN OTHER IMPURITIES ARE PRESENT.

100. Determination of Insoluble Matter.—Weigh 1 gram of the dry, finely powdered sample into a porcelain dish, cover it with a watch glass, moisten it with a few drops of cold water, and then cautiously add fuming nitric acid, drawing the cover aside slightly, and allowing the acid to run down the side of the dish. When violent action ceases, place on the water bath and heat with the cover on until red vapors are no longer given off. Then remove the watch glass, wash the particles that have spattered on it back into the dish, and evaporate to dryness. Moisten the residue with a little concentrate hydrochloric acid, heat it for a few minutes on the water bath, then add about 100 cubic centimeters of water, and heat to boiling. Allow the insoluble matter to settle, decant the clear liquid through a filter, and wash once by decantation with 40 or 50 cubic centimeters of boiling water. If the sample contains much lead, white crystals of lead chloride may be mixed with the insoluble matter; and in this case the precipitate must be boiled with water until they are dissolved. Then bring the precipitate on the paper and wash with hot water. Fold the filter around the precipitate, place them in a platinum crucible, and ignite gently at first, but finally heat strongly over a blast lamp. Cool in a desiccator, and weigh as insoluble silicious matter or gangue.

101. Determination of Lead.—If the sample contains lead, add about 10 cubic centimeters of one-third-strength sulphuric acid, and evaporate on the water bath until all the nitric acid is expelled. To the residue, add about 100 cubic centimeters of hot water, and, while heating on the water bath, stir with a glass rod until the precipitate appears perfectly white. Then stand aside in a rather warm place for the precipitate to completely settle. When the supernatant liquid has become perfectly clear, filter, and wash the precipitate several times with water containing 2 per cent. of sulphuric acid. Then remove the filtrate to a place of safety, set something under the funnel to catch the washings, and

wash the sulphuric acid out of the precipitate and filter with one-third-strength alcohol. These alcoholic washings may be thrown away. Dry the precipitate in an air bath, remove it as completely as possible from the paper, and cautiously burn the latter in a porcelain crucible. Moisten the ash with a drop of nitric acid and a drop of sulphuric acid, evaporate to dryness, and ignite gently to expel the excess of acid. When the crucible becomes cool, add the main precipitate, and ignite to dull redness for 5 minutes over a Bunsen burner. Cool in a desiccator, and weigh as lead sulphate $PbSO_4$.

102. Determination of Copper.—Evaporate the filtrate from the lead sulphate to from 100 to 150 cubic centimeters, or, if the sample does not contain lead, heat the filtrate from the insoluble matter to boiling. In either case, lead a rather rapid current of hydrogen sulphide through the gently boiling solution until the copper and cadmium are completely precipitated as sulphides and the precipitate settles rapidly. As soon as the precipitate settles, filter, and wash as rapidly as possible with water containing some hydrogen sulphide, protecting the precipitate from the air as much as possible to prevent oxidation.

Stand the filtrate aside for further examination and place a clean beaker under the funnel. Break the apex of the filter with a glass rod, and wash the precipitate into the clean beaker placed under the funnel, with about 30 cubic centimeters of a solution consisting of 1 part of concentrate sulphuric acid and 5 parts of water. In washing the precipitate from the filter, it is best to use a wash bottle with a very small tip in order to avoid using more than about 30 cubic centimeters of the acid mixture. When the precipitate is all washed into the beaker, cover it with a watch glass to prevent evaporation, and heat the mixture to boiling over a Bunsen burner. After boiling for a few moments, remove it from the flame and digest for an hour on a water bath. If any considerable quantity of the solution evaporates during this treatment, add sufficient water to replace that

driven off by the heat. Acid of this strength will completely dissolve the cadmium sulphide, but does not attack the sulphide of copper. After digesting for at least an hour on the water bath, filter off the copper sulphide, and wash it with pure water at first, and then with water containing hydrogen sulphide, taking care to expose the precipitate as little as possible to the action of air. Dry the precipitate in an air bath, remove it from the filter, and burn the latter in a Rose crucible. Add the precipitate, together with a little powdered sulphur, and ignite in a current of pure hydrogen as directed in Art. **18**, *Quantitative Analysis*, Part 1. Allow the precipitate to cool in a current of hydrogen, and weigh as cuprous sulphide Cu_2S.

103. Determination of Cadmium.—Dilute the acid filtrate from the copper sulphide to about 200 cubic centimeters, heat it on a water bath, and after it has assumed about the temperature of the bath, lead a rather rapid current of hydrogen sulphide through it until the cadmium is completely precipitated as sulphide, and the solution is thoroughly saturated with the gas. As soon as the precipitate settles, filter through a filter that has previously been dried in the air bath at 105°, for an hour, and weighed. Wash the precipitate at first with hydrogen-sulphide water that has been slightly acidulated with hydrochloric acid, and then with pure water. Dry the precipitate and filter in an air bath at 105° until a constant weight is obtained. This weight, minus the weight of the dry filter, is the weight of cadmium sulphide CdS.

104. Determination of Iron.—Boil the filtrate from the mixed sulphides of copper and cadmium, until the hydrogen sulphide has been completely expelled; then add sufficient concentrate nitric acid to oxidize the iron, and continue the boiling until the iron is completely oxidized. When the solution has become cool, neutralize it with a concentrate solution of sodium carbonate, stirring the solution continuously while adding the carbonate drop by drop until a slight permanent precipitate is formed. Then add 1 or 2 drops of

concentrate hydrochloric acid, and stir the solution for 2 or 3 minutes. If this does not dissolve the precipitate, add another drop of hydrochloric acid and again stir for 2 or 3 minutes. The precipitate must all be dissolved, but the solution should be kept as near neutral as possible. To this solution add a slight excess of sodium acetate, and boil it for a few moments, when the iron will be precipitated as basic ferric acetate, while the manganese and zinc remain in solution. As soon as the precipitate settles, filter it off and wash three or four times with hot water. If the iron precipitate is of any considerable size, it will almost invariably contain some manganese and zinc, and these must be removed. To do this, dissolve the partially washed precipitate in hot dilute hydrochloric acid, wash the filter well, heat the solution to boiling, and precipitate the iron with a slight excess of ammonia. Filter as quickly as possible, and wash the precipitate thoroughly with hot water. This filtrate will contain the manganese and zinc carried down with the iron, and is added to the main filtrate for further treatment.

Fold the filter around the precipitate, place them in a platinum crucible, and ignite gently at first, but gradually increase the temperature, and finally heat intensely over the blast lamp for 5 or 10 minutes. Cool in a desiccator, and weigh as ferric oxide Fe_2O_3.

105. Determination of Zinc.—If the addition of the second filtrate to the main filtrate produces a precipitate, dissolve it in a few drops of hydrochloric or acetic acid, and evaporate the combined filtrates to about 200 cubic centimeters. Slowly add sodium carbonate to this solution, while stirring it, until a permanent precipitate forms. Dissolve this in acetic acid, adding the latter until the reaction of the solution is decidedly acid. Heat the solution until it just begins to boil, and lead a rather rapid current of hydrogen sulphide through the gently boiling solution until the zinc is completely precipitated. Half an hour will usually suffice for this. As soon as the precipitate has settled, decant the clear liquid through a filter, and wash the precipitate by

decantation with hot water containing hydrogen sulphide and a little ammonium chloride. Then transfer the precipitate to the filter, and wash it with hot water containing hydrogen sulphide. Dry the precipitate in an air bath, remove it as completely as possible from the filter, and cautiously burn the latter in a Rose crucible. When cool, add the precipitate, together with a little powdered sulphur, and ignite in a stream of pure hydrogen, gradually increasing the temperature and finally heating for 10 minutes at the highest power of a Bunsen burner, but avoiding the use of a blast lamp. Allow the precipitate to cool in a current of hydrogen passing through the crucible, and weigh as zinc sulphide ZnS.

106. Determination of Manganese.—Evaporate the filtrate from the zinc sulphide to about 150 cubic centimeters, allow it to cool slightly, add 5 cubic centimeters of ammonium chloride, and then ammonium hydrate until the solution is very slightly alkaline. Wash the solution into a flask having a capacity of about 200 cubic centimeters, and precipitate the manganese as sulphide by adding a slight excess of ammonium sulphide. If the flask is not now full up to the neck, fill it with water, insert a stopper, and stand it in a warm place for 24 hours for the precipitate to collect and settle. Filter, and wash at first with water containing ammonium sulphide and ammonium chloride, and then with water containing ammonium sulphide alone. Dry the precipitate, remove it from the filter, and burn the latter in a Rose crucible. When cool, add the precipitate, sprinkle a little powdered sulphur over it, and ignite strongly over the blast lamp in a current of hydrogen in the same way that copper sulphide is ignited (see Art. **18**, *Quantitative Analysis*, Part 1). Allow the precipitate to cool in a current of hydrogen, and weigh as manganous sulphide MnS.

107. Second Method for the Separation of Zinc and Manganese.—Another method of separating the zinc and manganese in this analysis, which is largely used at the present time, is as follows: Evaporate the combined filtrates

from the iron precipitation to about 150 cubic centimeters, add sodium carbonate until a permanent precipitate forms, and dissolve this in acetic acid. Then add more sodium acetate, heat the solution nearly to boiling, add a saturated solution of bromine water until the liquid has a strong yellow color, and stand it on a water bath for an hour for the manganese to separate as hydrated oxide. Enough bromine must be added so that the solution will still be colored by it at the end of the hour. Now place the beaker on a gauze over a burner and heat carefully, finally boiling to expel the bromine. Allow the precipitate to settle, filter, and wash with water, taking care not to stir up the precipitate on the filter, or it may run through. Stand the filtrate and washings aside for the determination of zinc, and place a clean beaker under the funnel. Some of the manganese precipitate will usually cling to the beaker in which the precipitation was accomplished. Dissolve this in a small amount of sulphurous acid, to which a little hydrochloric acid is added, and pour this solution over the precipitate on the filter, thus dissolving it, and allowing the solution to run through into the clean beaker placed under the funnel to receive it. If this does not completely dissolve the precipitate, add a little more sulphurous acid to which a little hydrochloric acid has been added, and, when all is dissolved, wash the filter thoroughly with water, but keep the volume of the solution as small as possible. Boil the solution to expel the sulphur dioxide, add a slight excess of a solution of sodium-ammonium phosphate, and then to the gently boiling liquid add ammonium hydrate, drop by drop, while stirring constantly. As soon as a precipitate begins to form, stop the addition of ammonia, and stir vigorously with a glass rod until the precipitate, which is curdy at first, assumes a silky, crystalline appearance. Then add another drop of ammonia and again stir until the precipitate becomes crystalline. Continue this treatment until all the manganese is precipitated as white, crystalline manganese-ammonium phosphate. Then add 5 cubic centimeters of concentrate ammonia, stir well, and immediately stand the beaker in ice water to cool the

solution. When the liquid has become quite cold, stand it aside in a cool place for at least 2 hours for the precipitate to collect and settle. Filter, and wash the precipitate with a solution made by dissolving 10 grams of ammonium nitrate in 100 cubic centimeters of water, and adding a few drops of ammonium hydrate. Dry the precipitate in an air bath, remove it to a watch glass, and burn the filter in a porcelain crucible. When cool, add the precipitate, and ignite gently at first, but gradually increase the temperature, finally heating for 10 minutes at the full power of the blast lamp. Cool in a desiccator, and weigh as manganese pyrophosphate $Mn_2P_2O_7$.

Evaporate the filtrate set aside for the determination of zinc to 150 or 200 cubic centimeters. Add a concentrate solution of sodium carbonate to this solution, while stirring it continuously, until a slight permanent precipitate is formed. Dissolve this in a slight excess of acetic acid, heat the solution to boiling, and precipitate the zinc as sulphide by conducting a rather rapid current of hydrogen sulphide through it until the zinc is all precipitated and the solution is saturated with the reagent. As soon as the precipitate settles, filter as rapidly as possible, and wash with water containing a little ammonium nitrate and hydrogen sulphide, finally washing once with water containing only hydrogen sulphide. The addition of ammonium nitrate or ammonium chloride to the wash water, to keep the zinc sulphide precipitated from a hot acetic-acid solution from running through the filter, is seldom, if ever, necessary, but it does no harm, and may as well be added as a precaution. Dry the precipitate, remove it from the filter, and burn the latter in a Rose crucible. When cool, add the precipitate, together with a little powdered sulphur, ignite in a current of hydrogen, as directed in Art. **105**, and weigh as zinc sulphide ZnS.

108. Determination of Sulphur.—Weigh 1 gram of the pulverized mineral into a porcelain dish, moisten it with a few drops of water, and cover the dish with a watch glass. Draw the watch glass a little to one side, and add fuming nitric acid, drop by drop, until the further addition of acid no

longer produces any action in the dish. After allowing the dish to stand in a cool place for an hour, place it on a water bath and heat it gently until red fumes are no longer evolved. Then add a little concentrate hydrochloric acid, remove the watch glass, washing any particles that have spattered on it back into the dish, and evaporate the solution to dryness. Moisten the residue with hydrochloric acid, add 50 or 60 cubic centimeters of water, and heat to boiling to dissolve the residue. Filter off the gangue, and wash it thoroughly on the filter with hot water. Heat the filtrate to boiling and precipitate the sulphuric acid, formed by oxidizing the sulphur, with a moderate excess of barium chloride. Continue the boiling for a few moments after the precipitation is complete, and then stand in a warm place for 2 or 3 hours for the precipitate to separate completely. When the precipitate has settled, leaving the supernatant liquid perfectly clear, filter, and wash thoroughly on the filter with hot water. Dry the precipitate, remove it to a watch glass, and burn the filter in a porcelain crucible. Add a drop of nitric, and a drop of sulphuric, acid to the ash, evaporate to dryness, and ignite cautiously to expel the excess of sulphuric acid. When cool, add the precipitate, heat to dull redness, cool in a desiccator, and weigh as barium sulphate $BaSO_4$, which contains 13.73 per cent. of sulphur. On account of the well known tendency of barium sulphate to be reduced when ignited in the presence of paper, many chemists prefer to use a Gooch crucible for this determination. Many chemists also prefer to weigh the manganese pyrophosphate in a Gooch crucible, and this may be done by an experienced chemist, but it is best for a beginner to avoid heating phosphates in platinum vesssels, as there is always danger of the phosphorus attacking the platinum and injuring it.

CHALCOPYRITE.

109. Chalcopyrite is a double sulphide of copper and iron, having the composition Cu_2S, Fe_2S_3 or $CuFeS_2$, and is generally mixed with gangue. Some samples also contain

small quantities of cobalt, nickel, manganese, and zinc, and sometimes a sample is found that, in addition to these, contains lead, bismuth, arsenic, and antimony. A quantitative analysis should always be preceded by a careful qualitative examination, and the method of analysis adopted should be made to depend upon what is thus learned of the composition of the sample. If only the constituents usually present are contained in the mineral, they may all be determined in one sample, by using the following scheme:

In any event, select a small portion of the mineral that represents the average composition of the whole, pulverize it in an agate mortar, dry it in an air bath at a temperature ranging from 100° to 105°, and cool it in a desiccator.

110. Determination of Gangue.—Weigh 1 gram of the dry pulverized sample into a porcelain dish, mix it intimately with 3 grams of powdered potassium chlorate, cover the dish with a watch glass, and slowly add 40 cubic centimeters of concentrate nitric acid. Allow the dish to stand in a cool place for a few minutes, then place it on the water bath, and allow it to digest until the sample is completely decomposed, stirring the mixture frequently, and adding a little potassium chlorate from time to time. When decomposition is complete, remove the watch glass, wash any particles that may have spattered on it back into the dish, and evaporate to dryness. Add 10 or 15 cubic centimeters of concentrate hydrochloric acid to the residue, evaporate to dryness, and repeat the evaporation with concentrate hydrochloric acid two or three times. Moisten the dry residue with concentrate hydrochloric acid, add from 75 to 100 cubic centimeters of hot water, heat to boiling for a few moments, and filter off the insoluble matter as soon as it has settled. Wash thoroughly on the filter with hot water, wrap the paper around the precipitate, place it in a platinum crucible, ignite strongly over a blast lamp, cool in a desiccator, and weigh as insoluble matter or gangue.

111. Determination of Sulphur.—Heat the filtrate from the gangue to boiling, and precipitate the sulphuric

acid, formed by the oxidation of the sulphur, by slowly adding a solution of barium chloride in slight excess, while stirring the solution continuously. Continue the boiling for a few moments after a sufficient quantity of the reagent has been added, and then stand the beaker in a warm place for 3 or 4 hours for the precipitate to collect and settle. Filter, and wash the precipitate thoroughly with hot water. Dry the precipitate in an air bath, remove it as completely as possible from the filter, and burn the latter in a porcelain crucible. Moisten the ash with a drop of nitric acid and a drop of sulphuric acid, and ignite gently to drive off the excess of acid. When the crucible becomes cool, add the precipitate, heat to dull redness over a Bunsen burner, cool in a desiccator, and weigh as barium sulphate $BaSO_4$. From this weight, calculate the percentage of sulphur in the sample.

112. Determination of Copper.—Before precipitating the copper, the excess of barium chloride should be removed from the solution. To do this, heat the filtrate from the barium sulphate to boiling, and if the volume of the solution amounts to more than about 200 cubic centimeters, the boiling should be continued until the solution is reduced to about this amount. Then slowly add dilute sulphuric acid in slight excess to the boiling solution while stirring it continuously, and continue the boiling for a few moments after the reagent has all been added. Stand the solution in a warm place for a few hours for the precipitate to collect and settle; filter, and wash on the filter with hot water. The precipitate contains the excess of barium added to the solution, and may be thrown away.

Evaporate the filtrate to about 150 cubic centimeters, and, while keeping it as near the boiling point as possible, pass a moderately rapid current of pure hydrogen sulphide through it until the copper is completely precipitated as sulphide. As soon as the precipitate has settled, filter, and wash rapidly with water containing hydrogen sulphide, avoiding exposure to the air as much as possible. Dry the precipitate in an air bath, remove it to a watch glass, and

burn the filter in a Rose crucible. When the crucible is cool, add the precipitate, together with a little powdered sulphur, and ignite in a current of hydrogen. Allow the precipitate to cool in a current of hydrogen, and weigh as cuprous sulphide Cu_2S. From this weight, calculate the percentage of copper in the sample.

113. Determination of Iron.—Boil the filtrate from the copper sulphide until the hydrogen sulphide is completely expelled, add a little concentrate nitric acid, and continue the boiling until the iron is all oxidized to the ferric condition. Add about 15 cubic centimeters of ammonium chloride to the solution, and then slowly add ammonium hydrate in slight excess while stirring continuously. Continue the boiling for a moment after the precipitation is complete, then remove from the burner, and filter as soon as the precipitate has nearly settled. Wash the precipitate thoroughly on the filter with hot water, wrap the paper around it, place in a platinum crucible, heat gently at first to drive off the water and burn the paper, and then ignite strongly over a blast lamp. Cool in a desiccator, weigh as ferric oxide Fe_2O_3, and from this weight, calculate the percentage of iron in the sample.

The constituents already mentioned are the only ones contained in many samples, and in such cases the analysis is, of course, complete when this point is reached. Other samples, however, contain weighable quantities of zinc, cobalt, nickel, and manganese, and when the qualitative examination shows the presence of these, the analysis must be extended to include them.

114. Determination of Zinc.—Evaporate the filtrate from the iron precipitate to 100 or 150 cubic centimeters, add a strong solution of sodium acetate, and then acetic acid until the solution has a strong acid reaction. Heat the liquid to boiling, and while hot, pass a rather rapid current of hydrogen sulphide through it, thus precipitating the zinc, nickel, and cobalt, while the manganese remains in solution. As soon as the precipitate settles, filter, wash rapidly and

well with water containing hydrogen sulphide, and stand the filtrate aside for the determination of manganese. Dry the precipitate, remove it to a beaker, and burn the filter. Add the ash to the precipitate in the beaker, dissolve this in a little aqua regia, and evaporate the solution to dryness. Moisten the residue with hydrochloric acid and dissolve it in water. Add sodium carbonate to this solution drop by drop until a slight permanent precipitate forms, and dissolve this by adding a drop or two of hydrochloric acid, taking care to render the solution only faintly acid. Through this cold solution, lead a rather rapid current of hydrogen sulphide so long as the precipitate forms; then add a few drops of dilute sodium acetate, and continue to lead hydrogen sulphide into the solution until it is saturated with the gas.

During the precipitation of the zinc as sulphide, enough hydrochloric acid may be set free to prevent complete precipitation. When sodium acetate is added, hydrochloric acid unites with the sodium, forming sodium chloride, and setting free acetic acid, thus allowing the remaining portion of the zinc to be precipitated. Care must be taken not to add enough sodium acetate to unite with all the hydrochloric acid, or the cobalt and nickel will be precipitated as sulphides with the zinc.

After saturating the solution with hydrogen sulphide, cover the beaker and allow it to stand for 10 or 12 hours. If the directions have been carefully followed up to this point, the zinc will now be completely precipitated as sulphide, while the cobalt and nickel will remain in solution. Filter, and wash thoroughly with water containing hydrogen sulphide. Dry the precipitate in an air bath, remove it to a watch glass, and burn the filter in a Rose crucible. When the crucible is cool, add the precipitate, together with a little powdered sulphur, and ignite over a Bunsen burner in a current of hydrogen. Allow the precipitate to cool in a current of hydrogen, and weigh as zinc sulphide ZnS.

115. Determination of Cobalt.—Add a few drops of hydrochloric acid to the filtrate from the zinc sulphide, and

boil it till the hydrogen sulphide is expelled and the liquid is reduced to a small volume. Add a strong solution of potassium hydrate until the solution is slightly alkaline, render it slightly acid with acetic acid, then add a strong solution of potassium nitrite acidulated with acetic acid, and stand in a warm place for 24 hours for the precipitate of potassium-cobalt nitrite to separate. Filter, and wash the precipitate with a 10-per-cent. solution of potassium acetate to which a little potassium nitrite is added. Dry the precipitate in an air bath, and when dry, remove it to a porcelain dish. Burn the filter, and add the ash to the precipitate in the dish. Dissolve the precipitate in the least necessary quantity of hydrochloric acid, add a little water, heat the solution to boiling, precipitate the cobalt with a slight excess of sodium hydrate, and continue the boiling until the precipitate becomes dark colored, and of uniform texture. After allowing the precipitate to settle, filter, and wash thoroughly with hot water. Wrap the filter around the precipitate and ignite cautiously to burn off the paper. After the crucible has become cool, place the cover on it, lead in hydrogen until the air is all expelled, ignite in a current of hydrogen, and weigh as metallic cobalt.

116. Determination of Nickel.—Acidify the filtrate from the potassium-cobalt nitrite with hydrochloric acid, and boil it to expel the nitrous acid. Add ammonia to the solution until it is slightly alkaline, and then add acetic acid until it is just acid. Now add a few cubic centimeters of a strong solution of sodium acetate, heat to boiling, and conduct a rather rapid current of hydrogen sulphide into the boiling solution for 10 or 15 minutes. The nickel should now be completely precipitated as sulphide, and will settle rapidly. After allowing the precipitate to partially subside, add a strong solution of hydrogen sulphide to the clear supernatant liquid. If this produces a dark coloration, the nickel is not completely precipitated, and more hydrogen sulphide must be led into the solution to complete the precipitation. If no coloration is produced by the hydrogen-sulphide

solution, the precipitation is complete. In this case, as soon as the precipitate settles, filter, and wash well on the filter with water containing hydrogen sulphide, taking care to protect the precipitate from the action of air as much as possible. Dry the precipitate in an air bath, remove it to a beaker, burn the filter in a porcelain crucible, and add the ash to the precipitate. Digest the latter on a water bath with aqua regia, until the nickel sulphide is completely dissolved, and the separated sulphur appears pure yellow. Evaporate most of the excess of acid, dilute the solution with a small amount of water, and filter into a porcelain dish to remove the sulphur. Heat this solution to boiling, and precipitate the nickel with an excess of sodium hydrate. After a few moments, add bromine water a few drops at a time, while stirring constantly, until the precipitate becomes dark brown or black, and of uniform texture, taking care to keep the solution alkaline all the time. After allowing the precipitate to settle, filter, and wash thoroughly with hot water. Dry the precipitate, remove it as completely as possible from the filter, and burn the latter in a porcelain crucible. Add a drop or two of concentrate nitric acid to the ash, and evaporate to dryness. Then add the precipitate, ignite strongly, cool in a desiccator, and weigh as nickel oxide *NiO*.

117. Determination of Manganese.—Boil the filtrate from the mixed sulphides of zinc, cobalt, and nickel, to expel the hydrogen sulphide. Add sodium carbonate until the solution has an alkaline reaction, then render it slightly acid with acetic acid, and add a few cubic centimeters of a strong solution of sodium acetate. Heat this solution nearly to boiling, add a saturated solution of bromine water until the liquid has a strong yellow color, and heat it on the w bath for an hour. Then heat the solution over a Bu burner, finally boiling off the excess of bromine. Allow precipitate to settle, filter, and wash thoroughly with water containing 1 per cent. of hydrochloric acid, dire the jet of water around the top of the filter and taking

not to stir up the precipitate, or it may run through. Dry the precipitate, remove it as completely as possible from the filter, and burn the latter in a platinum crucible. Add the precipitate, ignite strongly for some time with the crucible uncovered, cool in a desiccator, and weigh as manganous-manganic oxide Mn_3O_4.

This method of determining manganese is quite largely used at the present time, and probably yields satisfactory results if only very small quantities of the metal are to be determined. If the manganese precipitate is large, however, it is very difficult to wash all of the alkali salts out of it, and to be sure of its state of oxidization when weighed. Hence, if the sample contains much manganese, it is much better to dissolve the precipitate of oxide produced by the bromine, in a mixture of hydrochloric acid and sulphurous acid, and precipitate the manganese from this solution as manganese-ammonium phosphate, as directed in Art. **107.** This method, to be sure, is much longer than the one just described, but it is also much more reliable, and, consequently, is to be recommended.

NATROLITE.

118. Natrolite is a hydrous silicate of alumina and soda, but in addition to these constituents, most samples contain small quantities of iron and calcium. It is best to make a qualitative analysis of the sample before commencing a quantitative analysis, and if any of the constituents mentioned in the following scheme are not contained in the sample, the parts of the method that relate to those constituents should be omitted.

The sample is prepared for analysis by grinding a small portion to an extremely fine powder, drying it in an air bath at 100°, and cooling it in a desiccator. The constituents usually determined are: silica, alumina, ferric oxide, lime (calcium oxide), soda, and water.

119. Determination of Silica.—Weigh about 1.5 grams of the dry, finely powdered sample into a porcelain dish, add 50 cubic centimeters of concentrate hydrochloric acid, cover the dish with a watch glass, and digest on a water bath, with frequent stirring, until the sample is completely decomposed. Then remove the watch glass, wash any particles that may have spattered on it back into the dish with a fine jet of water, and evaporate the solution to dryness on the water bath. When perfectly dry, remove it to an air bath, and heat it to 110° for an hour, to render the silica insoluble. Moisten the residue with a few drops of concentrate hydrochloric acid, add from 100 to 150 cubic centimeters of hot water, and boil for a few minutes to dissolve the chlorides of the metals. Allow the precipitate to settle, filter, and wash thoroughly with hot water. Wrap the filter around the precipitate, place in a platinum crucible, ignite gently to burn the paper and expel water, and then heat for several minutes at the highest power of the blast lamp. Cool in a desiccator, and weigh as silica SiO_2.

120. Determination of Alumina.—The filtrate from the silica is heated to boiling in a beaker of rather deep form, which should hold at least twice the volume of the solution, and the aluminum is precipitated as hydrate, by slowly adding to the gently boiling solution, a very slight excess of pure ammonium hydrate, while stirring the solution continuously. Continue the boiling about 1 minute after the precipitation is complete, taking care that the solution remains faintly alkaline, and then stand it aside a few minutes, for the precipitate to subside. As soon as the precipitate has settled, filter, and wash the precipitate thoroughly with hot water. Fold the filter around the precipitate, place in a platinum crucible, and ignite, gently at first, to drive off moisture and burn the paper, but finally at the full power of the blast lamp. Cool in a desiccator, and weigh as alumina Al_2O_3.

If the sample contains iron, it will be weighed with the alumina, and after making a separate determination of iron

oxide, as directed in Art. **124**, the weight found must be subtracted from the alumina precipitate, in order to obtain the correct weight and percentage of alumina.

121. Determination of Calcium.—Evaporate the filtrate from the alumina to about 150 cubic centimeters, add 3 or 4 drops of concentrate ammonia, and then add ammonium oxalate in limited quantity and but slight excess. Continue the boiling for a minute or so after all of the reagent has been added, and then stand in a warm place for several hours till the precipitate has completely settled. Filter, and wash the precipitate thoroughly with hot water, receiving the filtrate and washings in a porcelain dish. Wrap the filter around the precipitate, place them in a platinum crucible, and ignite gently to drive off water and burn the filter. Then heat the crucible at the highest power of the blast lamp for 15 minutes, cool in a desiccator, and weigh. Ignite again for 5 minutes at the highest power of the blast lamp, cool in a desiccator, and weigh again. If this weight is less than the first one, the precipitate must be heated again at the highest power of the blast lamp, and this must be repeated until a constant weight is obtained. The precipitate now consists of lime CaO, and the percentage in the sample is calculated from this weight.

This method of determining the calcium oxide is probably the most satisfactory under ordinary circumstances if only occasional analyses are made. If preferred, however, the calcium-oxalate precipitate may be moistened with concentrate sulphuric acid, heated very gently until the calcium is converted into sulphate and the carbon dioxide expelled, then ignited more strongly over a Bunsen burner, cooled in a desiccator, and weighed as calcium sulphate $CaSO_4$, as directed in Art. **40**, *Quantitative Analysis*, Part 1. Or, we may break the apex of the filter, then, with a mixture of sulphuric acid and water, wash the precipitate into a beaker, heat to about 75° and titrate with a standard solution of potassium permanganate, following the directions given in Art. **100**, *Quantitative Analysis*, Part 1.

122. Determination of Soda.—Evaporate the filtrate from the calcium oxalate to a small bulk in the porcelain dish, then transfer it to a platinum dish, washing the last portions of the solution in with a fine jet of distilled water, and evaporate to dryness. Place the dish in an air bath heated to about 100°, and gradually increase the temperature to about 150°. When all possibility of spurting is past, place the dish on a triangle, and cautiously heat it over a Bunsen burner until all ammonium salts are expelled, taking care to heat the dish to dull redness only, but making sure that every part of the dish is heated uniformly. When the ammonium salts are completely expelled, allow the dish to cool, and dissolve the residue of sodium chloride in a little water. Pour the solution through a small filter to remove any insoluble matter, and receive the filtrate in a weighed platinum dish, washing the sodium chloride out of the filter with the least necessary quantity of distilled water. Evaporate this filtrate to dryness, heat the dish to dull redness over the Bunsen burner after heating in the air bath to expel the last traces of water, cool in a desiccator, and weigh as sodium chloride $NaCl$. From this, calculate the percentage of soda Na_2O in the sample.

123. Determination of Water.—Grind a little of the sample to a coarse powder, dry it in an air bath at 100° and cool it in a desiccator. Weigh 2 or 3 grams of this coarse dry sample into a platinum crucible, and ignite carefully until a constant weight is obtained. The loss in weight is the weight of water, and from this, the percentage of water in the sample is calculated.

The crucible should be covered during ignition, and the sample used should be in the form of a coarse powder, as otherwise minute particles of the sample might be carried off with the water and thus yield erroneous results.

124. Determination of Iron.—If the qualitative examination has shown the presence of iron, this, of course, must be determined; and as the iron is precipitated in the

form of ferric oxide, with the alumina, the weight of ferric oxide found must be deducted from the weight of the alumina precipitate, before the percentage of alumina is calculated. Many chemists dissolve the alumina precipitate and determine the iron in this, but if this precipitate has been properly ignited, it is not entirely soluble in hydrochloric acid, and the writer prefers to determine the iron in a separate sample. Weigh from 1.5 to 3 grams of the dry, finely powdered sample into a porcelain dish, decompose it with concentrate hydrochloric acid in the same way that the original sample was decomposed, and evaporate to dryness. Moisten the residue with concentrate hydrochloric acid, add water, and heat to dissolve the chlorides of the metals. Filter off the silica, heat the filtrate to boiling, and precipitate the iron and alumina with a very slight excess of ammonia. Filter as soon as the precipitate settles, and wash once on the filter with hot water. Then remove as much as possible of the precipitate from the filter to a beaker or porcelain dish, stand this under the funnel, and dissolve the small quantity of precipitate adhering to the filter in a little hot, dilute hydrochloric acid, allowing this solution to run into the vessel containing the precipitate. Add a few more drops of hydrochloric acid to the filter, and wash all iron out of it with the least necessary quantity of water. Heat the vessel containing the precipitate and acid solution until the precipitate is dissolved, adding a little concentrate hydrochloric acid, if necessary. Wash this solution into a flask, reduce it with zinc, add sulphuric acid, and titrate with permanganate, following the directions given in Art. **95.**

From the weight of iron obtained by titration, calculate the weight and percentage of ferric oxide Fe_2O_3 in the sample. If the weight of the sample taken for the analysis is the same as the weight of sample taken for the determination of iron, the correction for alumina may be made by subtracting the weight of ferric oxide found, from the weight of the alumina precipitate. If different weights of sample are taken, the weight of ferric oxide in the alumina precipitate

must be calculated, by means of a proportion, or the percentage of ferric oxide found must be subtracted from the percentage of alumina and iron.

PREHNITE.

125. Prehnite is essentially a hydrous silicate of aluminum and calcium, but in addition to these constituents, most samples contain varying quantities of iron, manganese, and the alkalies. To prepare the sample for analysis, grind it to an exceedingly fine powder in a mortar, heat to 100° for 1 hour in an air bath, and cool in a desiccator.

Before commencing a quantitative analysis of the sample, it should be subjected to a qualitative examination, and if any of the constituents mentioned in the following method are not contained in it, those parts relating to such constituents should be omitted.

126. Determination of Silica.—Into a porcelain dish weigh about 1.5 grams of the dry, finely powdered sample, add 50 cubic centimeters of concentrate hydrochloric acid, cover the dish with a watch glass, and digest on the water bath till decomposition is complete, stirring the sample from time to time during this treatment. When decomposition is complete, remove the watch glass, wash back into the dish any particles that may have spattered on it during the decomposition, and evaporate the solution to complete dryness on the water bath. Heat the residue on the sand bath or in an air bath to render the silica insoluble, but take care not to heat it sufficiently to cause recombination of the silica and alumina. Moisten the residue with concentrate hydrochloric acid, add from 100 to 150 cubic centimeters of water, and heat gradually to boiling to dissolve the chlorides of the metals, leaving the silica as a precipitate. Filter, and wash the precipitate thoroughly with hot water. Wrap the filter around the precipitate, place them in a platinum crucible, ignite gently at first to drive off the water, and burn the paper, then raise the temperature and ignite at the full

power of the blast lamp for a few minutes. Cool in a desiccator, and weigh as silica SiO_2.

127. Determination of Alumina.—The filtrate from the silica is heated to boiling, in a beaker of rather deep form which should hold about twice the volume of the solution, and the alumina is precipitated by slowly adding ammonium hydrate—which must be free from carbon dioxide—to the gently boiling solution, while stirring continuously. Continue the boiling for a minute or so after precipitation is complete, taking care that the solution remains faintly alkaline. Then stand the beaker and contents aside for a few minutes for the precipitate to subside. As soon as the precipitate has settled, filter, wash once or twice with hot water, and stand the filtrate aside. The precipitate now contains all the alumina and iron—if there was any iron in the sample—together with part of the calcium, and probably some of the alkalies. These latter elements must be separated by reprecipitation. To do this, dissolve the precipitate in a small quantity of hydrochloric acid, dilute the solution to about 150 cubic centimeters, heat to boiling, and precipitate the alumina with a slight excess of pure ammonium hydrate in the same manner that the first precipitation was made. Filter, as soon as the precipitate settles, and wash thoroughly with hot water. Wrap the paper around the precipitate, place them in a platinum crucible, and, after heating gently to expel moisture and burn the paper, ignite for several minutes at the full power of the blast lamp. Cool in a desiccator, and weigh as alumina Al_2O_3.

If the sample contains iron, it will be precipitated and weighed with the alumina in the form of ferric oxide Fe_2O_3, and a correction must be made. The iron is determined as directed in Art. **124**, calculated to ferric oxide, and reported as such. The ferric oxide thus found is subtracted from the alumina precipitate, which also contains the iron, and the difference is pure alumina.

128. Determination of Calcium Oxide.—Unite the filtrates from the first and the second precipitation of

alumina, evaporate to 150 or 200 cubic centimeters, add a few drops of ammonium hydrate, and then slowly add to the gently boiling solution a slight excess of ammonium oxalate and a few more drops of ammonia. Continue the boiling for a few minutes and then stand in a warm place for 3 or 4 hours. Filter, wash the precipitate once or twice with hot water, and stand the filtrate aside. As prehnite contains a large percentage of calcium, a portion of the alkalies will frequently be carried down with this precipitate, and must be separated from it by reprecipitation. Dissolve the precipitate in the least necessary quantity of hydrochloric acid, dilute the solution to about 150 cubic centimeters, and heat it to boiling. To the gently boiling solution, slowly add ammonium hydrate in very slight excess; then add a few drops of ammonium oxalate solution and boil for a minute or two. After allowing the solution to stand in a warm place 3 or 4 hours for the precipitate to collect and settle, filter, and wash thoroughly with hot water. Wrap the filter around the precipitate, place them in a platinum crucible, and after heating gently to drive off water and burn the paper, ignite at the highest temperature of the blast lamp for 15 or 20 minutes, cool in a desiccator, and weigh quickly. Then ignite again for 5 minutes at the highest power of the blast lamp, cool, and weigh. If this weight varies appreciably from the first weight, the ignition must be continued until a constant weight is obtained, when the precipitate will be calcium oxide CaO.

If preferred, the calcium-oxalate precipitate may be converted into sulphate (see Art. **40,** *Quantitative Analysis*, Part 1), or the calcium oxide may be determined volumetrically, by means of potassium permanganate, as directed in Art. **100,** *Quantitative Analysis*, Part 1.

129. Determination of Manganous Oxide.—Unite the filtrates from the first and the second precipitation of calcium, and evaporate to about 100 cubic centimeters. Pour this solution into a flask that it will almost fill, add a few drops of ammonium sulphide, stopper the flask, and

stand it in a warm place for 24 hours for the precipitate of manganese sulphide MnS to collect and settle. Filter, and wash as rapidly as possible with water containing a very little ammonium sulphide. Excessive washing should be avoided.

Remove the filter containing the precipitate from the funnel to a beaker, add hydrochloric acid, and heat the mixture till the odor of hydrogen sulphide is no longer given off. Dilute the acid mixture with two or three times its volume of water, filter, and wash the residuary filter paper carefully, receiving the filtrate in a porcelain dish. Heat the filtrate to boiling; then remove the burner, and slowly add a solution of sodium carbonate, while stirring continuously, until the solution has a strong alkaline reaction. Boil a few minutes to expel carbon dioxide, allow the precipitate to settle, filter, and wash the precipitate with hot water until the washings are no longer alkaline to litmus paper. Dry the precipitate, remove it as completely as possible from the filter, and burn the latter in a weighed platinum crucible. When cool, add the precipitate, and heat over the blast lamp for 10 or 15 minutes, leaving the cover off of the crucible to freely admit the air, but taking care to avoid the action of reducing gases. Cool in a desiccator and weigh. The precipitate is now manganous-manganic oxide Mn_3O_4, and from this, the weight and percentage of manganous oxide MnO are readily calculated.

130. Determination of Potassium Oxide.—Acidify the filtrate from the manganese sulphide with hydrochloric acid, boil it until the odor of hydrogen sulphide is no longer given off, and filter to remove any sulphur that may have separated. Then evaporate the solution to dryness in a platinum dish, heat to about 150° in an air bath, and finally heat to dull redness over a Bunsen burner to expel ammonium salts, following the directions given in Art. **122.** Dissolve the residue in a little distilled water, and filter into a weighed platinum dish. Evaporate this solution to dryness, heat it in an air bath to about 150°, and finally heat it to dull redness over a Bunsen burner, taking care to heat

every part of the dish uniformly. Cool in a desiccator, and weigh quickly as soon as cool. The residue now consists of the chlorides of sodium and potassium.

Dissolve the residue of mixed chlorides in the least necessary quantity of cold water, add a strong solution of platinic chloride in sufficient quantity to convert all of the potassium and sodium into the double chlorides of these metals and platinum; and evaporate to a pasty consistence over a water bath in which the water is held as near the boiling point as possible. To the pasty mass in the platinum dish, add 35 or 40 cubic centimeters of 80-per-cent. alcohol, cover it with a watch glass, and stand it in a warm place for an hour or two, stirring from time to time. Decant the liquid through a weighed filter, wash once by decantation with 80-per-cent. alcohol, then transfer the precipitate to the filter, and wash thoroughly, but not excessively, with alcohol of the same strength. Dry the precipitate in an air bath at 130° for at least an hour, and longer if necessary. Weigh as potassium-platinic chloride K_2PtCl_6, and from this weight, calculate the weight and percentage of potassium oxide K_2O in the sample.

131. Determination of Sodium Oxide.—As sodium cannot be determined by precipitating and weighing it, when it is separated from potassium gravimetrically, it is always determined by difference. This is done as follows: From the weight of potassium-platinic chloride obtained, calculate the weight of potassium chloride KCl, and subtract this from the weight of the mixed chlorides of sodium and potassium previously obtained. The remainder would obviously be the weight of sodium chloride $NaCl$, and from this, the weight and percentage of sodium oxide Na_2O in the sample is readily calculated.

Instead of using the gravimetric method just described to separate sodium and potassium, the volumetric method described in Arts. **36** and **37** may be employed for this purpose.

132. Determination of Water.—If the sample is free from organic matter, the water of constitution may be

determined by weighing a convenient quantity of the dry sample in a crucible, igniting, and weighing again, when the loss will represent the water of constitution. But as many samples of prehnite contain organic matter, another method for the determination of water must frequently be employed. When organic matter is present, which is indicated by the sample becoming dark colored when heated, the following method is recommended. Take a piece of combustion tubing about 3 feet long, having an internal diameter of about ½ inch, heat it in the center by means of a blast lamp until it softens, draw the ends apart slightly, and then, keeping the two parts of the tube parallel, draw it out as shown in Fig. 10.

FIG. 10.

When cool, scratch the tube at the point *a* with a file, and break it off. Two tubes, each about 18 inches in length, are thus obtained. Heat the small end of one of these tubes in a blast-lamp flame until it fuses shut. By means of a glass rod push a little ignited asbestos loosely into the closed end of the tube, but do not pack it in tight. Then add enough pure powdered lead chromate to fill the tube for about 1 inch of its length. Next weigh out 1 gram of the dry, powdered sample, mix it intimately with 15 grams of fused and powdered lead chromate, and 1.5 grams of fused and powdered potassium bichromate, and introduce this mixture into the tube. Clean out the vessel (usually a mortar) in which these substances were mixed, by grinding two or three small portions of lead chromate in it, and charge these into the tube. Now lay the tube in a horizontal position, and, while holding the closed end up, rap it gently on the table to get a clear space along the top of the tube, for the free passage of gas or vapors, from one end of the tube to the other. Fit the open end of the tube with a singly perforated rubber stopper, and through the perforation pass one end of a U tube which is filled with dry calcium chloride and weighed. The tube will now appear as shown

in Fig. 11. Place the tube in a combustion furnace (see Fig. 14, *Organic Chemistry*, Part 1) and gradually turn on the burners, beginning at the closed end of the tube, *a*, Fig. 11. After the tube has been heated to redness throughout its entire length, turn out the burners next to the end *a*, and when

FIG. 11.

this has partially cooled, slip a piece of rubber tubing over the end *a* of the combustion tubing that was drawn out and sealed. Attach a drying tube filled with calcium chloride to the other end of the rubber tube, and then by means of a pair of pincers, break the tip *a* of the combustion tube, inside of the rubber tube. By means of a piece of rubber tubing slipped over *b*, attach the **U** tube to an aspirator, and draw about 1 liter of air through the apparatus. Turn out the lights, disconnect the apparatus, and weigh the **U** tube. The increase in weight is the weight of water in the sample.

Instead of using lead chromate and potassium bichromate, some chemists prefer gently ignited lead carbonate. The writer prefers the method as given above.

WOLFRAMITE.

133. Wolframite is a tungstate of iron and manganese, containing these metals in varying proportions. Its composition may be expressed by the formula $(FeMn)WO_4$, but in addition to these elements it frequently contains small quantities of calcium and magnesium. The mineral is very difficult to dissolve in acids, and, consequently, it is best to fuse it with alkaline carbonates in order to decompose it. The sample is prepared for analysis by grinding it to a powder in an agate mortar, heating it in an air bath at

about 110° to drive off any moisture, and cooling it in a desiccator.

134. Determination of Tungstic Oxide.—Weigh out 1 gram of the dry, finely powdered sample, mix it intimately with four times its weight of mixed carbonates (a mixture of equal parts of sodium and potassium carbonates) and introduce the mixture into a platinum crucible. Heat the crucible over a blast lamp until the contents are in a state of quiet fusion. Allow the crucible and contents to cool, and extract the fusion with hot water. Filter, and wash thoroughly with hot water. The tungsten will now be in the filtrate in the form of soluble sodium tungstate, while the insoluble residue contains the iron, manganese, calcium, and magnesium.

The tungsten may be separated from the filtrate in the form of tungstic acid or of mercurous tungstate. The second method is probably the one most generally used.

1. *Separation as Tungstic Acid.*—Render the filtrate acid with hydrochloric acid, evaporate to dryness on a water bath, and heat the residue to about 120° in an air bath for some time. Dissolve the alkaline chlorides in water and hydrochloric acid, filter, and wash the tungstic acid thoroughly on the filter with water containing hydrochloric acid. Dry the precipitate in an air bath, remove it as completely as possible from the filter, and carefully burn the latter in a weighed crucible, after moistening it with a saturated solution of ammonium nitrate. When the crucible cools, add the precipitate of tungstic acid, and ignite it with free access of air. Cool in a desiccator, and weigh as tungstic oxide WO_3. A constant weight must be obtained, and the precipitate should have a pure yellow color. If its color is not yellow, it should be moistened with a few drops of pure nitric acid, and again ignited with free access of air, cooled in a desiccator, and weighed.

2. *Separation of Mercurous Tungstate.*—To the alkaline filtrate, add a slight excess of nitric acid, so that, after driving out the carbon dioxide by heat, the solution has a

slight acid reaction. Stand this solution in a moderately warm place for 24 hours, and then add a solution of mercurous nitrate, and a little mercuric oxide HgO suspended in water. Allow the precipitate to completely subside, collect it on a filter, and wash it well with water containing mercurous nitrate. Dry the precipitate in an air bath, remove it as completely as possible from the filter, moisten the latter with a strong solution of ammonium nitrate, and burn it carefully in a weighed crucible. When the crucible becomes cool, add the precipitate and carefully ignite it with free access of air, under a hood or chimney with a strong draft. Cool in a desiccator and weigh as tungstic oxide WO_3. The ignition should be repeated until a constant weight is obtained. When this method is used, the precipitate should be ignited under a hood having a strong enough draft to carry off the mercury vapors.

135. Determination of Iron.—Dissolve the precipitate containing the iron and manganese—as well as calcium and magnesium if these were contained in the mineral—in hydrochloric acid. Heat the solution to boiling, add a few drops of concentrate nitric acid, and continue the boiling until the solution assumes a clear yellow color, showing that the iron is completely oxidized to the ferric state. When the solution becomes cold, dilute it moderately with cold water, and while stirring continuously, slowly add a solution of sodium carbonate until the solution assumes a deep reddish-brown color, but stop the addition before a permanent precipitate forms. If, by mistake, too much sodium carbonate is added, so that a precipitate that is not dissolved by stirring the cold solution for a minute or two is formed, add a drop or two of hydrochloric acid and stir until it dissolves, but keep the solution as near the neutral point as possible. To this cold solution, add a slight excess of sodium acetate and heat it to boiling for a few minutes. The iron will be precipitated as basic ferric acetate together with more or less manganese, depending largely upon the amount of sodium acetate added in excess of the amount required to

precipitate the iron. Probably 5 cubic centimeters of a cold saturated solution of sodium acetate will always be sufficient for this purpose, and the smaller the quantity added in excess of the required amount, the better.

Wash the precipitate three or four times in hot water, stand the filtrate aside, and dissolve the precipitate in hot, dilute hydrochloric acid. Dilute this solution moderately with cold water, and when cold, neutralize it with sodium carbonate, add sodium acetate, and precipitate by boiling as in the first instance. The precipitate should now contain only the iron, in the form of basic acetate. Filter as soon as the precipitate settles, and wash thoroughly on the filter with hot water. Wrap the filter around the precipitate, place them together in a platinum crucible, heat gently to drive off water and burn the paper, and then ignite strongly over the blast lamp. Cool the crucible and precipitate in a desiccator, and weigh as ferric oxide Fe_2O_3. From this weight, calculate the weight and percentage of ferrous oxide FeO in the sample.

136. Determination of Manganese.—Unite the filtrates from the two acetate precipitations of the iron, and if the bulk of the combined filtrates greatly exceeds 200 cubic centimeters, it should be concentrated to 150 or 200 cubic centimeters before proceeding. To this solution, add about 10 cubic centimeters of a saturated solution of sodium acetate, heat it nearly to boiling, and add pure bromine until the solution has a strong yellow color. Three or four cubic centimeters will be about the right amount. Heat the solution on the water bath for an hour, and if the clear liquid loses its yellow color during this time, add more bromine. Then boil the solution over a Bunsen burner to expel the excess of bromine, and stand it on a water bath for the precipitate of hydrated manganese dioxide to settle. Filter, and wash thoroughly with hot water, taking care not to stir up the precipitate, or it may run through the paper. When thoroughly washed, dissolve the precipitate in a mixture of sulphurous and dilute hydrochloric acids, receiving the solution in a clean beaker. When all is dissolved, wash the filter

thoroughly. Boil the solution to expel the sulphur dioxide, precipitate the manganese as manganese ammonium phosphate, by means of microcosmic salt, and after ignition, weigh it as manganese pyrophosphate, following the directions given in Art. **107.** From the weight of manganese pyrophosphate $Mn_2P_2O_7$ thus obtained, calculate the weight and percentage of manganous oxide MnO in the sample.

If the sample is a pure ferrous manganous tungstate, this will complete the analysis, but as most samples contain more or less calcium and magnesium, the analysis must generally be extended to include these elements.

137. Determination of Calcium.—To the filtrate from the manganese-dioxide precipitate, add ammonia until it is strongly alkaline, heat to boiling, and add a moderate excess of ammonium oxalate to precipitate the calcium. Continue the boiling for a few moments, and then stand the solution in a moderately warm place for 3 or 4 hours for the precipitate to collect and settle, taking care that the solution remains distinctly alkaline. Filter, and wash thoroughly with hot water containing a little ammonia. Wrap the filter around the precipitate, place them in a platinum crucible, and after heating gently to drive off moisture and burn the paper, ignite for 15 or 20 minutes at the highest power of the blast lamp. Cool in a desiccator, and weigh as calcium oxide CaO.

138. Determination of Magnesium.—Evaporate the filtrate from the calcium oxalate to a small bulk, cool it by standing the beaker in ice water, and precipitate the magnesium as magnesium-ammonium phosphate, by slowly adding a solution of microcosmic salt, while stirring the solution continuously. Add to the solution about one-fourth its volume of ammonium hydrate, stir it vigorously two or three times without allowing the stirring rod to touch the side or bottom of the beaker, and then stand it in a cold place for at least 6 hours for the precipitate of magnesium-ammonium phosphate to collect and settle. Filter, and wash the precipitate with hot water containing one-fourth its volume of ammonia. Dry it

in an air bath, remove the precipitate as completely as possible from the filter, and burn the latter in a weighed crucible. When cool, add the precipitate, ignite intensely over a blast lamp, cool in a desiccator, and weigh as magnesium pyrophosphate $Mg_2P_2O_7$. From this weight, calculate the weight and percentage of magnesium oxide MgO in the sample.

FELDSPAR.

139. Feldspar is a silicate of aluminum, potassium, and sodium, and usually contains smaller quantities of the oxides of iron, calcium, and magnesium. It is not decomposed by acids, and consequently must be fused. This necessitates working on two samples, for the alkalies cannot be determined in the portion fused with sodium and potassium carbonates for the determination of the other elements, and the other constituents cannot be determined accurately in the portion treated for the alkalies.

As a number of other substances have much the same composition as feldspar, the method here given may be used in a number of instances by modifying it slightly to suit each particular case. For instance, ordinary mica contains the same constituents as feldspar, but in somewhat different proportions; and the same may be said of sandstone and ordinary glass, except that these may also contain manganese oxide. This statement cannot be made to include all varieties of glass, however, for different varieties vary in their composition. For instance, flint glass contains considerable lead, and but little calcium, lead oxide being substituted for calcium oxide in this variety.

Great care must be taken in the preparation of a sample of feldspar for analysis, for the mineral is very difficult to decompose. It should be ground in an agate mortar, in small portions at a time, until it is so fine that no gritty particles can be felt with the pestle. This powder is then dried in an air bath for an hour at about [illegible] and cooled in a desiccator.

140. Determination of Silica.—Mix 1 gram of the dry, powdered sample with about 6 grams of mixed carbonates (equal parts of sodium and potassium carbonates) in an agate mortar, and introduce this mixture into a 50-gram platinum crucible. Rinse out the mortar with about 2 grams of the mixed carbonates and pour this on top of the mixture in the crucible. Cover the crucible, and heat gently over a Bunsen burner at first, then gradually raise the temperature to the full power of the blast lamp, and maintain this heat till the contents of the crucible have been in a state of quiet fusion for some time. Turn out the gas, and cool quickly by at once standing the crucible on a large clean plate of cold metal. The hot crucible is usually handled by means of the crucible tongs shown in Fig. 12. When partly cooled,

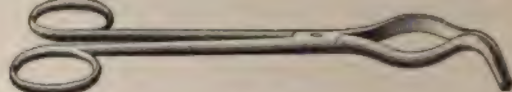


FIG. 12.

the crucible may be dipped into ice water, but care must be taken not to allow any water to get inside of the crucible. When cooled quickly in this way, the fusion may generally be removed from the crucible without difficulty, as soon as cold.

Invert the crucible in a porcelain dish, and tap it gently, when the fusion will usually fall out in the dish. Leave the fusion and crucible both in the dish, add about 75 cubic centimeters of water and heat to boiling. Then cover the dish with a watch glass and slowly add hydrochloric acid until the liquid has a strong acid reaction and the fusion is dissolved. Remove the crucible from the dish and wash it off by means of the wash bottle, allowing the washings to run into the dish. Wash the watch glass off into the dish, and then evaporate the solution to dryness on the water bath, stirring frequently towards the last. When quite dry, pulverize the residue with a small agate pestle, and brush any of the residue that may adhere to the pestle back into

the dish by means of a camel's-hair brush. Then place the dish and contents in an air bath and heat it at 120° to 125° for 2 hours, to render the silica insoluble. After the residue has become cool, add 30 cubic centimeters of concentrate hydrochloric acid, and digest it on a water bath for about half an hour. Then add 100 cubic centimeters of water, and heat to boiling for 10 or 15 minutes over a Bunsen burner to dissolve the chlorides of the metals. Filter, and wash thoroughly with hot water. The washing should be continued until the wash water comes through the filter free from hydrochloric acid. Suck the precipitate and filter as dry as possible by means of the filter pump, wrap the filter around the precipitate, place them in a platinum crucible, and, after heating gently to drive off water and burn the paper, ignite at the full power of the blast lamp. Cool in a desiccator, and weigh as silica SiO_2.

141. Determination of Iron and Alumina.—Concentrate the filtrate from the silica to 150 or 200 cubic centimeters, heat it to boiling, and precipitate the iron and alumina by adding a very slight excess of ammonia to the gently boiling liquid, while stirring it continuously. Continue the boiling for a few moments, but be sure that a faint odor of ammonia can still be observed. Filter as soon as the precipitate settles, preferably while the liquid is still warm, and wash thoroughly with hot water. Suck the precipitate and filter as dry as possible by means of the pump, wrap the filter around the precipitate, place them in a platinum crucible, and after driving off moisture and burning the paper at a gentle heat over the Bunsen burner, ignite intensely over the blast lamp. Cool in a desiccator, and weigh as the oxides of aluminum and iron $Al_2O_3 + Fe_2O_3$.

Fuse the precipitate with about eight times its weight of acid potassium sulphate, heating the fusion until the second molecule of sulphuric acid is expelled, leaving the normal sulphate. When cool, add a volume of pure, concentrate sulphuric acid, equal to that of the fused mass, and heat cautiously until the contents of the crucible become fluid.

When cool, place the crucible in a porcelain dish containing hot water, and digest over a low flame until the contents of the crucible are completely dissolved. Transfer the solution to a flask, add about 15 cubic centimeters of pure, dilute sulphuric acid and 10 grams of granulated zinc, place a small funnel in the mouth of the flask and stand in a moderately warm place until the iron is reduced. Filter the solution through a large folded filter, wash this by filling it with cold water and allowing it to run through into the main solution, and titrate at once with potassium permanganate.

It is necessary in this case to make a blank determination to ascertain the amount of permanganate consumed by substances other than the iron in the sample. This is done as follows:

In a clean platinum crucible place the same weights of acid potassium sulphate and sulphuric acid as were used in fusing the precipitate of iron and alumina, and cautiously heat until the bisulphate is dissolved. After allowing this to cool, take it up in water, transfer the solution to a flask, add the same amounts of zinc and sulphuric acid as were used in the regular determination, place a small funnel in the mouth of the flask, and allow this solution to stand the same length of time as the main solution. Filter, wash the filter paper, and titrate with potassium permanganate. Deduct the volume of permanganate consumed by the blank from the amount used in the regular determination; the remainder is the amount used in oxidizing the iron in the sample. From this, calculate the weight and percentage of ferric oxide Fe_2O_3 in the sample. The weight of Fe_2O_3 thus obtained, subtracted from the weight of $Al_2O_3 + Fe_2O_3$, gives the weight of aluminum oxide Al_2O_3 in the sample, and from this, the percentage is calculated.

Instead of fusing the precipitate of iron and alumina with acid potassium sulphate in order to determine the iron, some chemists prefer to fuse a fresh portion of the original sample with mixed carbonates, filter off the silica, precipitate the iron and alumina as in the regular analysis, dissolve this precipitate in the least necessary quantity of hydrochloric

acid, reduce the iron, and titrate with permanganate, following the directions given in Art. **95.**

142. Determination of Calcium.—If the filtrate from the iron and alumina exceeds about 200 cubic centimeters, as will usually be the case, evaporate it to about this bulk. Then to the boiling solution, add a moderate excess of ammonium oxalate and 10 or 15 cubic centimeters of ammonium hydrate, and continue the boiling for a few minutes, stirring continuously to prevent bumping. Stand the solution in a warm place for at least 4 hours for the precipitate of calcium oxalate to separate. Filter and wash thoroughly with hot water containing a little ammonia. Suck the precipitate and filter as dry as possible by means of the filter pump, wrap the filter around the precipitate, place them in a platinum crucible, and after heating gently to expel moisture and burn off the paper, ignite for 15 or 20 minutes at the full power of the blast lamp. Cool in a desiccator, and as soon as cool, weigh quickly. Then reignite for 5 minutes at the highest temperature of the blast lamp, cool in a desiccator, and weigh. This must be repeated until a constant weight is obtained, when the precipitate will be calcium oxide CaO.

143. Determination of Magnesium.—Evaporate the filtrate from the calcium to 150 or 200 cubic centimeters, and cool it by standing the beaker containing it in ice water. When cold, add a moderate excess of microcosmic-salt solution $HNaNH_4PO_4$ and 35 or 40 cubic centimeters of ammonia. Stir the solution vigorously for some time, taking care not to let the stirring rod strike the side of the beaker, and then stand it aside in a cool place for at least 6 hours for the precipitate of magnesium-ammonium phosphate to form and settle. Filter, and wash the precipitate thoroughly with a mixture of 1 part of ammonia and 3 parts of water, containing 50 grams of ammonium nitrate to the liter. Dry the precipitate, remove it as completely as possible from the filter, and cautiously burn the latter in a porcelain

crucible. When cool, add the precipitate, and ignite at a gradually increasing temperature, finally heating strongly over the blast lamp. Cool the precipitate in a desiccator and weigh as magnesium pyrophosphate $Mg_2P_2O_7$. From this weight, calculate the weight and percentage of magnesium oxide MgO in the sample.

144. Determination of Alkalies.—The best method for the determination of the alkalies in insoluble silicates, and the one generally employed, was proposed by Dr. J. Lawrence Smith. Dr. Smith devised an excellent crucible and burner for this purpose, but as the cost of this apparatus is considerable, an ordinary platinum fusion crucible is frequently employed in its stead, and serves the purpose very well.

Accurately weigh .5 gram of the finely pulverized sample into a large agate or glazed porcelain mortar, add an equal weight of pure ammonium chloride, and grind the two together intimately. Then to the contents of the mortar, add a weight of pure calcium carbonate equal to eight times the weight of the sample, in three or four successive quantities, mixing intimately after each addition. During the mixing the mortar should stand on a piece of glazed paper to catch any particles that may fly out. When thoroughly mixed, pour the contents of the mortar on the glazed paper, and from this transfer it to the platinum crucible. Rinse out the mortar by grinding a little more calcium carbonate in it, pour this on the glazed paper, and from the paper transfer it to the crucible, thus making sure of getting all the sample in the crucible. Tap the crucible gently on the table to settle the contents down, cover it, and place it on the triangle in a slanting position, as shown in Fig. 5, except that the crucible should remain closely covered. Bring a Bunsen burner with the flame turned low under the crucible, so that the flame strikes about the top of the mixture, and heat it to faint redness. Turn the crucible from time to time so that each part is equally heated, and gradually move the burner towards the bottom of the crucible.

When fumes of ammonium chloride are no longer given off, turn the flame higher, and heat for an hour, turning the crucible and moving the burner from time to time to be sure that all parts of the mixture are subjected to the same temperature. Too intense an ignition should be avoided, as it is likely to vitrify the mass too much. A dull-red heat is sufficient. After allowing the crucible to cool, the contents will be found agglomerated in a semifused mass, which may be removed by tapping the crucible.

By inverting the crucible in a porcelain dish and gently tapping it, or by cautiously using a stirring rod, if necessary, remove the mass to the porcelain dish. Wash any particles that may adhere to the crucible into the dish with hot distilled water, wash off the crucible lid in the same way, and then continue the addition of distilled water until about 80 cubic centimeters have been added. Cover the dish with a watch glass, and heat the contents to boiling over a Bunsen burner. The mass will usually slake and crumble like lime in a few minutes. If it should not, cautiously grind it up in the dish by means of an agate pestle, and digest it on a water bath until it is completely slaked.

If the mass should be hard to detach from the crucible, do not use much force in trying to remove it, or the crucible may be injured, but fill the crucible to about two-thirds its capacity with water, heat it nearly to boiling, and let it stand a short time, when the mass will slake and may be washed out.

Filter, and wash the precipitate until a few drops of the washings, acidified with nitric acid, give only a slight cloudiness when treated with silver nitrate. About 200 cubic centimeters of water will be required for this washing. The filtrate now contains the potassium and sodium in the form of chlorides, together with ammonium chloride and some calcium chloride formed in the operation. All that remains is to separate the calcium as carbonate, and volatilize the ammonium chloride, in order to obtain the chlorides of sodium and potassium free from other elements. This is done as follows:

Dissolve about 1.5 grams of pure ammonium carbonate in water, and add this to the filtrate, thus precipitating all the calcium as carbonate. Do not filter at once, but place the solution containing the precipitate on a water bath, and evaporate it to about 50 cubic centimeters. Then add a little more pure ammonium carbonate and a few drops of ammonium hydrate, to reprecipitate any calcium dissolved by the action of the ammonium chloride on the calcium carbonate. Bring the solution just to boiling, filter through a small filter, and wash the precipitate with the least necessary quantity of water. Add a few drops of ammonium carbonate and a drop or two of ammonium hydrate to the filtrate, and, if a precipitate forms, filter it off. Evaporate the solution to dryness on a water bath, preferably in a platinum dish; dissolve the residue in the least necessary quantity of water, and add a few drops of ammonium carbonate and a drop or two of ammonium hydrate to precipitate any calcium that may thus far have escaped precipitation. Filter, and wash with a small volume of water, receiving the filtrate in a weighed platinum dish. Evaporate to dryness on a water bath, then place the dish in an air bath heated to 100°, and gradually raise the temperature to 150° to expel all the water and avoid danger of spattering when more strongly heated. Place the dish on a triangle, and heat it over a Bunsen burner, moving the burner from place to place in order to heat each part of the dish equally. Heat the dish to faint redness until the ammonium chloride is completely expelled, but avoid a higher temperature, lest some of the sodium and potassium chlorides be volatilized. When ammonium salts are completely driven off, cool in a desiccator, and weigh as $KCl + NaCl$. Dissolve the residue in the least necessary quantity of water, precipitate the potassium as potassium-platinic chloride, and from the weight of this obtained, calculate the weight and percentage of potassium oxide K_2O in the sample. Then, from the weight of potassium-platinic chloride, calculate the weight of potassium chloride, and by subtracting this weight from the weight of the mixed chlorides, obtain the weight of sodium chloride. From this,

calculate the weight and percentage of sodium oxide Na_2O in the sample, following the directions given for the separation of the alkalies in Arts. **130** and **131.**

145. Loss on Ignition.—Although feldspar does not normally contain water of constitution, many samples dried at 110° lose weight when subjected to a higher temperature. This loss in weight is sometimes reported as water, but as it may be due to other things, and as the loss is not great enough to be of sufficient importance to justify an examination as to its cause in each case, it has become customary to report it as *loss on ignition.* The determination is made as follows:

Weigh into a platinum crucible 2 or 3 grams of the pulverized sample, which has been dried at 110°, heat it over a Bunsen burner for 20 minutes, cool in a desiccator, and weigh again. From the loss in weight, calculate the percentage of loss.

The sample used for this determination does not need to be as finely powdered as those used for the fusions. In fact, it is best to have this sample a little coarser, as there is then less danger of particles of it being carried out of the crucible by the draft during ignition.

QUANTITATIVE ANALYSIS.

(PART 3.)

IRON ANALYSIS.

GENERAL REMARKS.

1. Thus far the work in quantitative analysis has been confined to the determination of single elements in chemical compounds of known composition, and to the complete analysis of substances, in both of which cases a student could check his work: in the first instance, by calculating the theoretical percentage of the element sought, in the compound analyzed; and in the second, by adding together the ercentages of the different constituents found, to see how ear the sum of the constituents approaches 100 per cent.

In *Quantitative Analysis*, Part 1, we endeavored to escribe the most approved methods of determining the rincipal elements in a way that would give the student a good eneral idea of the methods of quantitative work, and, at e same time, some experience in the determination of the lements most frequently met. In Part 2, the knowledge btained in Part 1 is put in practice in the analysis of a few ypical compounds, alloys, and minerals, chosen with a view o rendering the student familiar with the general methods f analysis.

In a work of this character it would be impossible to

§ 18

describe the analysis of every existing compound, alloy, and mineral, and no attempt has been made to do so. Instead of this, we have attempted, by means of a few typical examples, to render the student so familiar with the different processes that he can readily apply his knowledge in all similar cases; and, if he has worked faithfully on his papers up to this point, he should now be able to analyze any compound, alloy, or mineral likely to be met.

The following work, which deals with technical analysis, is built up largely on the same principles as the preceding, but differs from it in several respects. As a rule, a complete analysis is not required, but merely the determination of some of the constituents, generally those on the percentage of which the value or quality of the substance depends. Hence, in much of the succeeding work the accuracy of the results cannot be determined by the methods previously employed, and, except in the case of determinations that are made daily, the results should always be checked by making duplicate determinations. In the laboratories of manufacturing establishments where a chemist determines the same elements in many samples every day, it would generally be impossible to make duplicate determinations in each case, and it is hardly necessary, for he soon becomes so familiar with his routine work that he is not likely to make a mistake; but even in these cases, it is a good plan to make duplicate determinations if time permits, and any determination outside of the regular work should always be checked by a duplicate.

So many methods are employed in iron and steel works chemistry at the present time that it would be impossible to describe them all in this Paper. Consequently, only one or two methods, as a rule, will be given for the determination of each element. In the case of elements for the determination of which several methods are largely employed, one strictly accurate method and one or two of the more rapid methods will generally be described. In experienced hands most of these short or rapid methods will yield extremely accurate results with most samples, and, on account of their

rapidity—enabling a chemist to do a great deal of work and to obtain results in a short time—they are used almost exclusively in iron and steel works laboratories. As some of them do not give accurate results in all cases, it is necessary for the iron-works chemist to be familiar with longer methods that will yield exact results in every case, and, for this reason, both short and long methods are described.

IRON ORES.

2. As iron ore is the principal "raw material" in the manufacture of iron, its analysis will be treated first. This is an important matter, for the value of the ore depends on its composition Other things being the same, the value of an ore depends on the amount of iron it contains, but the percentage of iron is not the only consideration, for other constituents have much to do with fixing its value for certain uses. Thus, an ore containing much phosphorus, however rich in iron it may be, would be unsuited for the production of pig iron to be used in the manufacture of Bessemer steel, because the phosphorus in the ore would pass into the steel and render it unfit for use.

An analysis is not only useful in determining the value of an ore, but also to determine the quantity of other material that is to be charged into the furnace with it. Thus, the amount of limestone added to form a slag with impurities depends on the amount of impurity to be "slagged off." The principal determinations in the analysis of iron ores are *insoluble matter* and *silica*, *iron*, *phosphorus*, *sulphur*, *manganese*, and sometimes *water*.

3. Selection and Preparation of a Sample.—The selection of a sample is a matter of importance, for, if the results of the analysis are to be of any value, a sample must be chosen that accurately represents the whole quantity of which the analysis is supposed to show the composition.

In order to obtain such a sample, the following points

should be observed: the relative amount of fine ore and lumps in the lot to be sampled should be carefully noted, and this proportion must be observed in the sample taken. In sampling lumps, it is not sufficient to break pieces from the surface, but the lump should be broken, and pieces taken from both the exterior and interior, for a lump seldom has the same composition throughout. As the heavy particles that naturally find their way towards the bottom seldom have the same composition as the lighter material near the top, portions of the sample should be drawn from different parts of the lot. The fine ore should be taken up in portions amounting to about a teaspoonful, and the pieces of lumps should be about the size of cherries.

This sample will usually be too large for laboratory use, and a smaller sample must be obtained from it. Just how this is done is not a matter of importance so long as the sample obtained represents the composition of the whole quantity, but probably the best method, and the one most frequently used, is that known as quartering. This is accomplished as follows:

Break up the lumps of ore until the largest pieces are about the size of buckshot, mix the whole sample thoroughly, place it in a conical pile, and then flatten this pile. Mark the pile into quadrants, by means of a stick, as shown in Fig. 1, by passing two lines at right angles to each other through the center of it. Then remove two alternate quarters and throw them aside. Thus considering the quadrants as numbered consecutively from *1* to *4*, Nos. *1* and *3* would be discarded, and Nos. *2* and *4* saved, or vice versa. The quadrants to be discarded may be removed by means of a spatula, shown in Fig. 2. The quadrants left are now thoroughly mixed, made into a conical pile, and the operation is repeated until a sample

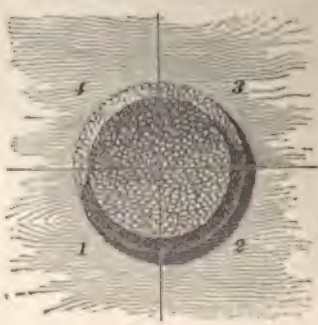


FIG. 1.

of suitable size for the laboratory is obtained. If the sample contains lumps of sufficient size to cause danger of getting a final sample that does not represent the whole lot of ore, it should be broken up finer during the operation. When a sample of the proper size is obtained, it is ground to

FIG. 2.

a coarse powder and mixed thoroughly. Although a cast-iron mortar and pestle are largely used in breaking up and grinding iron ores, they are totally unfit for this purpose, for the iron, especially of the pestle, rapidly wears away, and, becoming mixed with the ore, gives it a fictitious value in iron. A mortar and pestle of hardened steel, or a chilled-iron bucking board and muller, shown in Fig. 3, answer the purpose much better.

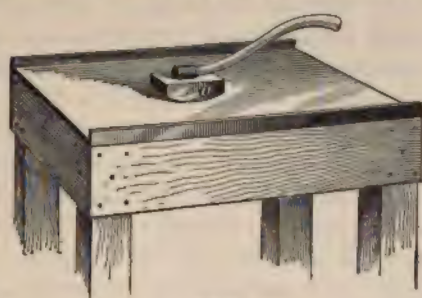


FIG. 3.

The treatment of the ore from this point on differs in different laboratories. Some furnacemen want to know the exact composition of the ore as it is purchased and charged into the furnace, while others want to know the composition of the dry ore, and the chemist must regulate his method of treatment to suit the particular case. The following method probably gives the most thorough knowledge of the composition of the ore, but where such complete knowledge is not desired, the treatment may be shortened. In any case, if the moisture is to be taken into account, the ore should be ground and quartered quickly, as wet ores will lose some of their water during the operation, if much time is spent, and dry ores may take up some moisture from the atmosphere.

WATER.

4. Determination of Hygroscopic Water.—Spread the ore out on a clean piece of paper, and weigh about 50 grams of it into a watch glass or other suitable vessel, dipping portions from different parts of the sample by means of a spatula. Care should be taken to dip to the bottom of the sample each time, for however well mixed it may be, this coarsely powdered sample will scarcely be uniform, the heavier portions that tend to sink to the bottom seldom having the same composition as the lighter portions on top. Place the weighed sample in an air bath, and heat it at a temperature ranging from 100° to 105° C., until it ceases to lose weight. To be sure of obtaining accurate results, this drying should be continued for 10 or 12 hours, though in many cases the water will all be driven off in much less time. When a constant weight is obtained, the loss in weight is the weight of hygroscopic water, and from this the percentage of water in the sample is obtained.

If only an analysis of the dry ore, or of the ore as it comes from the mine, is required, this determination may be omitted, and the other determinations proceeded with, either at once, or after drying, as the case may be. If this method is followed, however, by working on the same sample after it is dry, the percentage of water in the original sample and the percentage of other constituents in the dry ore are obtained; and, from these figures, the percentage of each of the constituents in the wet ore may readily be calculated.

INSOLUBLE MATTER AND SILICA.

5. Grind the sample used for the determination of water in an agate mortar until it is fine enough to pass through a sieve having 100 meshes to the linear inch, commonly called a 100-mesh sieve. The whole must be passed through the sieve, for the hard particles that resist crushing seldom have the same composition as the easily pulverized portion. As soon as powdered, the sample should be placed in a bottle and tightly stoppered.

Weigh 1 gram of this sample into a porcelain dish, add 20 cubic centimeters of concentrated hydrochloric acid, cover the dish with a watch glass, and boil very gently on a hot plate or sand bath until the ore appears to be completely decomposed. A hot plate is merely a thin iron plate placed on a suitable support and heated by a burner; and a sand bath is made by placing some sand in an iron basin and heating it in the same way.

When the sample appears to be decomposed, remove the watch glass, wash any particles that may have spattered on it back into the dish, and evaporate to dryness. Or, if the solution has a tendency to bump, evaporate to dryness with the watch glass on. This requires more time, but is necessary in some cases to avoid loss by spattering. When dry, heat the residue until the odor of hydrochloric acid is no longer given off, but avoid a very high temperature. Allow the residue to cool, add about 10 cubic centimeters of concentrate hydrochloric acid, and boil for a few moments. Then add 30 or 35 cubic centimeters of water, and continue the boiling for a few minutes to dissolve all the soluble matter. Filter, preferably with suction, wash thoroughly with dilute hydrochloric acid and water alternately, and, finally, two or three times with water. Suck the precipitate and filter as dry as possible, wrap the filter around the precipitate, place them in a platinum crucible, and, after heating gently to drive off moisture and char the paper, ignite intensely over the blast lamp. Allow the crucible to become cool, and weigh as *insoluble matter* or *silicious residue*, as it is sometimes called.

To the insoluble matter in the crucible, add about ten times its weight of "fusion mixture," made by mixing equal parts of the carbonates of sodium and potassium, and heat over the blast lamp till all is in a state of quiet fusion. Run the fusion well up on the sides of the crucible, and then cool it rapidly by dipping the crucible into a porcelain dish containing about 50 cubic centimeters of pure cold water, taking care not to get any water in the crucible at first. When the fusion becomes cool enough so that there is no further danger

of spattering, turn the crucible on its side, cover the dish with a watch glass, and heat to boiling, so as to partially dissolve the fusion. Remove the dish from the flame, and complete the solution by cautiously adding concentrate hydrochloric acid until the liquid has a strong acid reaction. Remove the crucible, wash it off thoroughly, letting the washings run into the dish, evaporate to dryness on a sand bath or hot plate, and heat at a moderate temperature to render the silica insoluble. When cool, add 10 cubic centimeters of concentrate hydrochloric acid and 30 or 40 cubic centimeters of water to the residue, and boil a few minutes to dissolve the soluble matter. Filter and wash thoroughly with hot water to remove all alkaline salts from the filter. Wrap the filter around the precipitate, place them in a platinum crucible, and, after heating gently to expel moisture and char the paper, ignite intensely over a blast lamp. Cool, and weigh as silica SiO_2.

IRON.

6. There are two methods of determining iron in ores in very general use, known as the bichromate and the permanganate methods. The permanganate method gives a very distinct end reaction, but as permanganate is decomposed by hydrochloric acid or chlorine, precautions must be taken to render harmless the hydrochloric acid used to dissolve the ore, before titrating the solution. Hydrochloric acid and chlorine do no harm when the bichromate method is used; hence, the ore may be dissolved in hydrochloric acid, the solution reduced by stannous chloride, and this may be titrated at once with bichromate. As each method has its advantages, they are both largely used. A method of dissolving an ore in hydrochloric acid, reducing with stannous chloride and titrating with permanganate, has recently been devised, and is being quite largely used at the present time, in some places. As it has several advantages, it will probably be more generally adopted in time, and consequently all three methods will be described.

7. The Bichromate Method.—Weigh 1 gram of the sample into a beaker, add 20 or 25 cubic centimeters of concentrate hydrochloric acid, cover the beaker with a watch glass, and digest on a sand bath for several hours, at a temperature very near the boiling point, until the ore appears to be completely decomposed. From .2 to .5 gram of potassium chlorate is frequently added at this point to oxidize any organic matter that may be present. Now raise the temperature and boil the solution very gently until its volume is reduced to about 10 cubic centimeters. With nearly all ores, the iron will now be completely dissolved, and the residue will be light colored. It should be examined, however, and if reddish, or very dark, it should be treated as described later.

If the residue is white, remove the watch glass and wash it off into the beaker, washing down the sides of the beaker at the same time, and using a quantity of water about double the volume of the solution. Then slowly add a solution of stannous chloride from a pipette or burette to the hot solution until it is colorless, indicating that the iron is all reduced to the ferrous condition, and add 2 or 3 drops in excess to be sure that reduction is complete.

After a little experience has been acquired, it is easy to tell by the appearance of the solution when reduction is complete, but at first it is best to test the solution by means of potassium sulphocyanide. To do this, place a drop of potassium-sulphocyanide solution on a white porcelain plate, known as a *spot plate*, dip a small drop of the iron solution from the beaker on the end of a stirring rod, and mix it with the drop of sulphocyanide on the plate. If a red color is produced, it shows that the solution still contains ferric iron, and more stannous chloride must be added. If it shows no color, or only a faint pink tint, the reduction is complete.

Pour the reduced solution into a rather large beaker, wash the small beaker thoroughly, adding the washings to the solution, and dilute this to 300 or 350 cubic centimeters with pure cold water. Then add about 25 cubic centimeters of a saturated solution of mercuric chloride all at once, stir the

solution, and titrate with potassium bichromate, running the bichromate in until a drop of the solution, removed to a spot plate by means of a stirring rod, and mixed with a drop of pure potassium-ferricyanide solution, does not produce a blue color for 20 or 30 seconds. The operation should be conducted as rapidly as possible from the time the iron is reduced, for, if allowed to stand for any considerable time, it will be partially reoxidized by the action of the air.

The mercuric chloride is added to destroy the excess of stannous chloride, which, if left free in the solution, would reduce some of the bichromate, and thus yield an erroneous result. If it is added quickly, as directed, it will form a white, silky precipitate that does not in any way interfere with the titration, but if added gradually, a gray or black precipitate of metallic mercury is produced, and the solution must be thrown away, for such a solution will not yield reliable results. If the bichromate is standardized so that 1 cubic centimeter oxidizes .01 gram of iron, and exactly 1 gram of sample is taken, each cubic centimeter of the solution used will represent 1 per cent., and each tenth of a cubic centimeter will represent one-tenth of 1 per cent. of iron in the sample. Many chemists, however, prefer to standardize the bichromate solution so that 1 cubic centimeter of it oxidizes .005 gram of iron; and when this is done, .5 gram of ore is usually taken for the determination. If this is done, the reading in cubic centimeters will represent the percentage of iron, the same as in the first instance.

If the residue left when the ore is dissolved is strongly colored, and exact results are required, the following method should be employed: Dilute the solution slightly so that the hydrochloric acid will not destroy the paper, filter, and wash, receiving the filtrate in a beaker, which should now be covered and stood aside. Place the filter and residue in a platinum crucible, burn off the paper and fuse the residue with about ten times its weight of mixed carbonates of sodium and potassium. Dissolve the fusion in water and hydrochloric acid, filter out the insoluble matter, and wash thoroughly with dilute hydrochloric acid and water. Heat the filtrate

to boiling, add a few drops of concentrate nitric acid, and precipitate the iron with a slight excess of ammonia. Filter, dissolve the precipitate in a mixture composed of equal parts of concentrate hydrochloric acid and water, and add this solution to the main solution of iron. Heat this nearly to boiling, reduce it with stannous chloride, dilute with water, add mercuric chloride, and titrate with bichromate as directed above.

8. The Ordinary Permanganate Method.—Weigh 1 gram of the dry, finely powdered ore into a beaker, add 15 or 20 cubic centimeters of concentrate hydrochloric acid, cover the beaker with a watch glass, and digest on a sand bath or hot plate at a temperature very near the boiling point, until the ore appears to be completely decomposed. This may be accomplished in 15 or 20 minutes, or may require several hours, depending on the ore. If time permits, the sample is generally allowed to digest for several hours in any case to insure complete decomposition. If the ore contains organic matter, a little potassium chlorate should be added to destroy it, and some chemists add it to all ores as a precautionary measure. Probably the majority of ores yield all their iron to this treatment, but if the insoluble residue contains iron, it must be filtered off, fused, and treated as in the determination of iron by the bichromate method.

When decomposition is complete, unless the bulk of solution is considerably reduced, it should be boiled gently until the volume of the solution amounts to rather less than 10 cubic centimeters. Violent boiling should be avoided, as some ferric chloride may thus be volatilized from a concentrate solution. Dilute the solution with about 30 cubic centimeters of water, and, if a large residue remains, it is generally filtered off, washed thoroughly with hot water, and the filtrate and washings are collected in a flask that has a capacity equal to three or four times the volume of the solution. The residue may be fused or discarded, depending on whether it contains iron or not. The practice at this point differs, however. Some chemists prefer to filter every sample, while

others never filter the solution unless the residue contains iron, but simply wash the contents of the beaker into the flask.

In any case, to the solution in the flask add about 10 grams of pure granulated zinc, and place a small funnel in the mouth of the flask. This will catch fine drops of liquid that are carried up with the evolved hydrogen, and will protect the solution from air, while it allows the hydrogen to escape. When the reaction slackens, heat the solution gently to cause as much as possible of the acid to unite with the zinc, forming zinc chloride, which does not interfere with the titration. If a basic-iron salt begins to separate when the acid is nearly all taken up by the zinc, dissolve it in the least necessary quantity of hydrochloric acid, adding the acid drop by drop.

To the solution, which should now contain but a very small amount of free hydrochloric acid, add about 30 cubic centimeters of dilute sulphuric acid, and allow the action of the acid on the zinc to proceed for a few moments, and the iron will all be reduced. It is best, at first, to test the solution by removing a drop of it on a stirring rod, and mixing it with a drop of potassium-sulphocyanide solution previously placed on a spot plate, but after a little experience, this will be unnecessary. Pour the solution through a large fluted filter, and wash the filter by filling it once or twice with pure cold water, receiving the filtrate and washings in a large beaker or porcelain dish. Dilute this solution to 300 or 400 cubic centimeters with cold water, and titrate at once with potassium permanganate.

Many chemists do not filter the solution from the zinc, but add an excess of dilute sulphuric acid, and after the zinc is all dissolved, wash the solution into a beaker or porcelain dish, dilute, and titrate as above. When this is done, there is always danger of small particles of zinc being washed into the dish, and generating hydrogen during titration. As the hydrogen thus generated will reduce some of the permanganate, and thus yield an erroneous result, the writer prefers to filter out the zinc. The results may be obtained more quickly, and, if the filtration is performed as above directed,

the solution is not exposed to the air sufficiently to cause oxidation. By taking up most of the hydrochloric acid with zinc, and titrating the iron in a dilute solution containing considerable free sulphuric acid, the injurious effect of hydrochloric acid is overcome, and the end reaction is as sharp as if no hydrochloric acid were present.

9. The Modified Permanganate Method.—It has been found that by using a so called *titrating mixture* to counteract the evil effects of hydrochloric acid, iron may be reduced with stannous chloride and titrated with permanganate. The chief advantage of this method is the rapidity with which it yields results. Its principal disadvantage is the fact that in the hands of an inexperienced operator, the results may not be accurate, as it requires more skill and experience to make a determination correctly by this method than by either of the methods previously described. As this method is chiefly used where results must be obtained quickly, and as stannous chloride appears to aid in dissolving the ore, a little less of this than the amount required to reduce the iron is usually added at the beginning of the operation, but this is not essential. The process as usually carried out is as follows:

Weigh 1 gram of ore into a small beaker, add about 15 cubic centimeters of concentrate hydrochloric acid and a small amount of stannous chloride (about 5 cubic centimeters for ordinary ores), cover the beaker, and heat on a sand bath or hot plate until the ore is decomposed, but avoid vigorous boiling. If the ore contains organic matter, a little potassium chlorate should be added, and the heating continued until the chlorine and oxide of chlorine are expelled. Wash the cover and sides of the beaker with a jet of water from a wash bottle to bring every particle of iron into the solution, using 15 or 20 cubic centimeters of water for this purpose. Heat this solution nearly to boiling and add stannous chloride from a pipette or burette until the solution becomes colorless, showing that the iron is reduced, but avoiding the addition of more than 2 or 3 drops in excess. It is a good plan to test

this solution, to learn when reduction is complete, by removing a drop of it to a spot plate and mixing it with a drop of potassium sulphocyanide.

When the iron is all reduced, wash the solution into a large beaker or a porcelain dish with cold water, and dilute to about 100 cubic centimeters with cold water. The solution should now be quite cool. Add to it 15 cubic centimeters of mercuric chloride all at once, and stir it vigorously. Then add 50 cubic centimeters of titrating mixture (see Art. **15**), and again stir vigorously. Dilute the solution to about 600 cubic centimeters with cold water, and titrate with potassium permanganate as quickly as possible. The end reaction is a faint pink color, which must be noted quickly, as it is of short duration.

SOLUTIONS FOR IRON DETERMINATIONS.

10. Standardizing Permanganate and Bichromate Solutions.—The methods of standardizing potassium-permanganate and bichromate solutions by the use of ferrous ammonium sulphate, have been given in Arts. **94** and **97**, *Quantitative Analysis*, Part 1, and it is the writer's experience that solutions thus prepared yield accurate results when working on ores, provided a blank determination is made, and the amount of standard solution reduced by reagents, as determined by this blank, is deducted from the reading in each case. Most chemists, however, prefer to standardize solutions against a sample of iron, steel, or ore, the iron contents of which has been carefully determined. Piano wire is largely used for this purpose, but a standard ore has the advantage that standardization and titration are carried on under the same conditions, and in exactly the same manner. The course to be pursued in standardizing a solution for the determination of iron, by any of the methods commonly used, would readily suggest itself from what has been said on this subject in Arts. **94** and **97**, *Quantitative Analysis*, Part 1, but in order to make it more clear the method employed when a standard ore is used is given.

Dissolve the potassium permanganate or bichromate in

water, making sure that all is in solution, and then dilute until 1 liter contains, approximately, 6 grams of permanganate or 8.8 grams of bichromate, as the case may be. Mix the solution thoroughly, and, after it has stood for at least 24 hours, standardize it as follows: Dissolve exactly 1 gram of the standard ore, which we will suppose contains exactly 50 per cent. of iron, reduce the solution and titrate with the solution being prepared, following the directions given in Art. **7** for a bichromate solution, or those given in Art. **8** for a permanganate solution. Suppose 49 cubic centimeters of the solution is required to oxidize the iron in the 1-gram sample; then, each 49 cubic centimeters of this solution must be diluted to 50 cubic centimeters in order that 1 cubic centimeter shall oxidize .01 gram of iron. If the volume of the solution amounts to, say, 950 cubic centimeters, the calculation would be: $49 : 50 = 950 : x = 969.4$ cubic centimeters, the required volume, or $969.4 - 950 = 19.4$ cubic centimeters of water must be added. This should not be added all at once, however, for fear of rendering the solution too dilute. It should be diluted nearly to the calculated amount and a second determination made with the standard ore. Then dilute to the exact calculated amount, and check the solution by means of a third determination. It is always best to make duplicate determinations each time when standardizing.

If a standard solution of bichromate is to be made of such strength that 1 cubic centimeter equals .005 gram of iron, it should be diluted until 1 liter contains about 4.4 grams of the pure salt, and .5-gram samples of the standard ore should be used in the determinations. After standardizing the solutions, they should be kept in tightly stoppered bottles in a cool dark place, and should be restandardized every two weeks, as they gradually change in strength owing to slow decomposition or to other causes. It is a good plan to weigh out a sample of the standard ore, and run it with other samples at frequent intervals. Any change in the strength of the solution will thus be detected.

In iron-works laboratories, where many determinations are

made, several liters of the standard solutions are generally made up at a time. The method of preparation is, of course, the same as in the case of smaller quantities. Many chemists do not standardize their solutions so that 1 cubic centimeter oxidizes exactly .01 gram of iron, but make a solution having approximately this strength, and determine the value in iron of 1 cubic centimeter of it. Then, by multiplying the number of cubic centimeters used by the value of 1 cubic centimeter, the amount of iron is obtained, but where many determinations are made, it is an advantage to have the solution of such strength that the percentage of iron may be read directly from the burette.

11. Stannous Chloride.—Different chemists make the stannous-chloride solution, used to reduce the iron, of different strengths, varying from 25 to 150 grams of the dry salt to the liter. A very good solution for this purpose is made by dissolving 80 grams of pure stannous chloride in 500 cubic centimeters of concentrate hydrochloric acid and 500 cubic centimeters of water. The stannous chloride used for this solution should be pure and fresh, for the salt slowly decomposes on standing and forms an insoluble compound. If a pure fresh sample of the salt is not at hand, the solution may be made by dissolving pure metallic tin in concentrate hydrochloric acid and diluting to the proper volume with pure water. If this is done, it is best to place a piece of platinum foil in contact with the tin, to promote solution, which is very slow at best.

12. Mercuric Chloride.—The mercuric-chloride solution, used to oxidize the excess of stannous chloride is generally made by dissolving 50 grams of the salt in 1 liter of water. This makes very nearly a saturated solution, and the reagent is frequently made by adding water to a little more of the salt than it will dissolve, thus keeping a little undissolved salt in the bottle. If this is done, the solution should be shaken up frequently to keep the undissolved salt from forming a hard cake that is not readily dissolved in water.

13. Potassium Sulphocyanide.—The potassium-sulphocyanide solution, used in testing for ferric iron, to learn when reduction is complete, is made by dissolving from 5 to 10 grams of the salt in 100 cubic centimeters of water.

14. Potassium Ferricyanide.—The potassium-ferricyanide solution, used as an indicator in determining iron by the bichromate method, is made by dissolving about .5 gram of the pure solid ferricyanide in 100 cubic centimeters of water. The ferricyanide must be free from ferrocyanide, for this gives a blue color with ferric iron. It may be tested by mixing a drop of it with a drop of ferric solution that is known to be free from ferrous compounds. This solution is slowly reduced by the light, and, consequently, a fresh solution should be made up every day, or at least every second day.

15. Titrating Mixture.—To make the titrating mixture, used when iron is reduced by stannous chloride and titrated with permanganate, dissolve 160 grams of manganous sulphate in water and dilute the solution to 1,750 cubic centimeters; then add 330 cubic centimeters of 85-per-cent. phosphoric acid, and, finally, stir in 320 cubic centimeters of sulphuric acid of 1.84 Sp. Gr. By using this mixture, iron may be titrated with permanganate in a cold dilute solution containing hydrochloric acid, and satisfactory results obtained, if the titration is performed rapidly.

PHOSPHORUS.

16. As the percentage of phosphorus varies greatly in different ores, and as ores differ in solubility, the exact method employed for the determination of this element varies with different ores. Another cause of variation in the details of the method, is the fact that, while, as a rule, exact results are required, it sometimes happens that rapidity is of more importance than extreme accuracy, and in such cases the method is shortened to suit the conditions. As exact results are usually required, a very accurate method

is here described, and if the student should need a more rapid method at any time, he can readily work out a method that will meet his requirements, after studying the determination of phosphorus in iron and steel. In working out a shorter method, the student should remember that the solution from which the ammonium phospho-molybdate is precipitated should have as near as possible the same composition in every case, for the composition of this precipitate varies slightly in different solutions, and if the solution is too strongly acid, the phosphorus will not be completely precipitated; while from an alkaline solution it will not be precipitated at all.

If the ore contains a very high percentage of phosphorus, 1 gram of the sample should be used for this determination, while with ores containing a very low percentage of this

FIG. 4.

element, 10 grams are usually taken. The quantity of acid used to dissolve the ore varies with the amount of sample taken, but not in a direct proportion. To dissolve 1 gram of ore, 25 cubic centimeters of acid should be used, while 100 cubic centimeters will be sufficient for 10 grams. This

determination usually proves a stumbling block to the beginner, and, consequently, the directions should be followed as closely as possible until the student becomes familiar with it. After a little practice, however, it becomes very easy to obtain extremely accurate results. The details of the method as used for ordinary ores are as follows:

Weigh 5 grams of the finely powdered sample into a porcelain dish, add 1 cubic centimeter of nitric acid and 75 cubic centimeters of concentrate hydrochloric acid, cover the dish with a watch glass, and digest on a sand bath, a hot plate, or on a tripod placed over an Argand burner, shown in Fig. 4, until the ore appears to be completely decomposed. Then evaporate to dryness, and, to render the silica insoluble, ignite the residue at a moderate temperature until the odor of hydrochloric acid is no longer perceptible. When the residue becomes cool, add 50 cubic centimeters of concentrate hydrochloric acid, heat gently until the mass dissolves, then raise the temperature and boil the solution down to about 20 cubic centimeters. Add 30 cubic centimeters of water, boil for a few moments, filter off the insoluble matter, wash thoroughly with hot water, and stand the filtrate aside. The insoluble residue will seldom contain more than a trace of phosphorus, and, with most ores, in cases where rapidity is of greater importance than extreme accuracy, it may be discarded. As a rule, however, it should be treated as follows:

Place the filter and residue in a platinum crucible and burn off the paper, mix the residue with five or six times its weight of the mixed carbonates of sodium and potassium, and heat till all is in a state of quiet fusion. After cooling, dissolve the fusion in water and hydrochloric acid, and evaporate to dryness in a porcelain dish. Moisten the residue with concentrate hydrochloric acid, again evaporate to dryness, and ignite gently until the odor of hydrochloric acid can no longer be observed. When cool, add from 5 to 10 cubic centimeters of concentrate hydrochloric acid to the residue, heat gently for a few moments, then add 25 cubic centimeters of water, heat to boiling, and filter. Heat the

filtrate to boiling, add a few drops of concentrate nitric acid, and then a slight excess of ammonium hydrate. Any phosphorus that may have remained in the insoluble residue will be carried down in the precipitate thus formed. Filter, wash two or three times with hot water, dissolve the precipitate in the least necessary quantity of hydrochloric acid, and add this solution to the main filtrate, which will now contain all the phosphorus originally in the sample.

Evaporate this solution in a porcelain dish until it becomes syrupy, and the scale of iron oxide that forms on the sides of the dish is only dissolved slowly, but take care not to evaporate the solution until a scale forms that is not dissolved by agitating the solution. Now remove the dish and contents from the flame, immediately add 7 or 8 cubic centimeters of concentrate nitric acid, and, after rotating the dish a few times to mix the solution, wash down the watch glass and sides of the dish with water. Transfer the solution, which must not contain any undissolved matter, to a flask of about 700 cubic centimeters capacity, and wash out the dish, using water enough to bring the volume of the solution up to about 100 cubic centimeters.

To this solution add 30 cubic centimeters of concentrate ammonia, and, after giving the flask a rotary motion to mix the contents, dissolve the precipitate in concentrate nitric acid, adding about 2 cubic centimeters in excess of the amount actually required to give a clear solution. Insert a thermometer in the solution, bring its temperature to exactly 85°, add 75 cubic centimeters of ammonium-molybdate solution, and agitate the mixture for 5 minutes by giving the flask a sharp rotary motion. The phosphorus is thus completely precipitated as ammonium phospho-molybdate, generally known as *yellow precipitate*, which, when precipitated as directed above, contains 1.63 per cent. of phosphorus. Allow the precipitate to settle, which will usually require 15 or 20 minutes, but do not allow it to stand more than 1 hour. Filter and wash the precipitate with water acidified with nitric acid until the iron is completely removed, filling the filter from six to ten times.

The precipitate is next dissolved in ammonia. It is best to dissolve it on the filter and allow the solution to run through into a clean beaker and wash the filter thoroughly. If the silica and iron have been thoroughly removed, as directed above, this is not necessary, however, and the precipitate may be washed into a beaker and dissolved in ammonia. In either case, bring the volume of the solution to about 80 cubic centimeters, add magnesia mixture in considerable excess, and dissolve the precipitate formed in the least necessary quantity of hydrochloric acid. Stand the beaker containing the solution in ice water and slowly add concentrate ammonia while stirring the solution vigorously.

After the solution is rendered alkaline, add about 25 cubic centimeters of concentrate ammonia, stir vigorously and stand aside in a cool place for at least 3 hours for the precipitate to collect and settle. It is a good plan to allow it to stand overnight. Filter, wash the precipitate thoroughly with a dilute solution of ammonia (1 part of concentrate ammonia to 3 parts of water) containing 5 grams of ammonium nitrate in each 100 cubic centimeters of solution, and dry it in an air bath. Remove the precipitate as completely as possible from the filter and burn the latter in a platinum crucible. When cool, add the precipitate, ignite strongly over the blast lamp, cool in a desiccator, and weigh. The precipitate will now generally consist of pure magnesium pyrophosphate $Mg_2P_2O_7$, which contains 27.93 per cent. of phosphorus, but as a little silica may be present, it is best to make a correction as follows:

Fill the crucible to half its capacity with nitric acid of 1.2 Sp. Gr., apply heat until chemical action ceases, and, if an insoluble residue remains, filter it off, wash thoroughly, ignite strongly in a platinum crucible over the blast lamp, and weigh. By deducting this weight from that of the original precipitate, the weight of magnesium pyrophosphate is obtained, and from this the percentage of phosphorus is calculated.

As the percentage of phosphorus in the ammonium phospho-molybdate, precipitated as above directed, is known, this

precipitate may be weighed or titrated by one of the methods described for the determination of phosphorus in iron or steel; but as the gravimetric method in which the phosphorus is finally weighed as magnesium pyrophosphate is the only one that yields exact results in every case, this method should be employed whenever extreme accuracy is required.

SOLUTIONS FOR PHOSPHORUS DETERMINATIONS.

17. Ammonium Molybdate Solution.—There are many formulas for making this solution, and several of these that the writer has tried have proved very satisfactory. The following formula, proposed by Mr. E. F. Wood, is a very good one, and is handy in laboratories where large quantities of the solution are used. If the student wishes to make up a smaller amount of the solution, he can use smaller quantities of the constituents, keeping the proportion the same, of course.

Mix 1 pound of pure molybdic acid with 1,200 cubic centimeters of water, add 700 cubic centimeters of concentrate ammonium hydrate (.90 Sp. Gr.) and stir until all is dissolved. Then slowly add 300 cubic centimeters of nitric acid of 1.42 Sp. Gr. to partly neutralize the excess of ammonia. In each of four 5-pound (2½-liter) bottles, place a mixture of 500 cubic centimeters of nitric acid of 1.42 Sp. Gr., and 1,200 cubic centimeters of water. Into each of these bottles slowly pour 550 cubic centimeters of the ammonium-molybdate solution just prepared, meanwhile agitating the contents of the bottle continuously. In laboratories having an air blast, the agitation may be accomplished by passing a current of air through the solution. When all is added, stand the solution in a warm place for 24 hours, and decant the clear solution, or filter before using.

18. Magnesia Mixture.—The magnesia mixture for this purpose is frequently made as follows: Dissolve 110 grams of pure crystallized magnesium chloride and 280 grams of ammonium chloride in 1,300 cubic centimeters of

water. To this add 700 cubic centimeters of ammonia of .96 Sp. Gr., shake well, allow to stand several days, and filter before using.

19. Nitric-Acid Wash.—To make the dilute nitric acid used in washing the "yellow precipitate," measure 15 or 20 cubic centimeters of concentrate nitric acid (Sp. Gr. 1.42) into a wash bottle, fill up to 1 liter with pure water and shake well. The solution is generally made to contain 20 cubic centimeters of nitric acid to the liter, but some chemists prefer a more dilute solution.

SULPHUR.

20. Sulphur occurs in iron ores both in the form of sulphides and sulphates. It must all be obtained in the form of a soluble sulphate, and precipitated as barium sulphate by means of barium chloride. In the case of most ores, the sulphur may be obtained in the form of a soluble sulphate, either by treating the ore with hydrochloric and fuming nitric acids, or by fusing it with the mixed carbonates of sodium and potassium and potassium nitrate. The fusion method is the only one that yields accurate results in all cases, but as the treatment with acids is the handiest in cases where it is admissible, both methods are given.

21. The Aqua-Regia Method.—Weigh 5 grams of the ore into a rather deep porcelain dish, cover it with a watch glass, and slowly add 20 cubic centimeters of fuming nitric acid. When the action nearly ceases, add 30 cubic centimeters of concentrate hydrochloric acid, and allow it to stand at the temperature of the laboratory for a short time—an hour or two, if time permits. Transfer to a water bath or a sand bath, and digest at a gentle heat until the ore appears to be decomposed. Then add 1 gram of sodium carbonate dissolved in 10 cubic centimeters of water, raise the temperature, and evaporate to dryness. In order to render the silica insoluble, moisten the residue with concentrate hydrochloric acid,

again evaporate to dryness, and ignite gently until the odor of hydrochloric acid is no longer given off.

When cool, add 10 cubic centimeters of concentrate hydrochloric acid, heat for a few moments, then add 50 cubic centimeters of water and boil till solution is complete. Filter off the insoluble matter, and wash with hot water until the soluble material is completely removed from the paper, and the volume of the solution amounts to from 150 to 200 cubic centimeters. Heat the solution to boiling, add a moderate excess of barium chloride (25 cubic centimeters of a 5-per-cent. solution is sufficient for most ores), and continue the boiling for several minutes. Stand the solution on a water bath or other warm place for an hour, then stand it in a cool place till the precipitate has completely settled and the solution is cool.

Filter, preferably, through a Gooch crucible. When the solution has run through, fill it up with hot water, and when this has run through, wash once with hot dilute hydrochloric acid, and then wash thoroughly with hot water. Suck the water out of the asbestos as completely as possible, dry, and ignite it at a dull-red heat for 5 minutes, cool in a desiccator, and weigh as barium sulphate $BaSO_4$, which contains 13.73 per cent. of sulphur. If a filter paper is used instead of a Gooch crucible, the precipitate should be removed from it as completely as possible, and the paper burned cautiously before the precipitate is ignited.

22. The Fusion Method.—Mix 1 gram of the pulverized ore with about 6 grams of sodium and potassium carbonates, and .5 gram of potassium nitrate; introduce this mixture into a large platinum crucible and cover it with a mixture of about 2 grams of the mixed carbonates, and .25 gram of potassium nitrate. Cover the crucible and heat it at a gradually increasing temperature until the mass is in a state of quiet fusion, but do not ignite longer than necessary, as this mixture is likely to injure the crucible if the heating is continued too long. Run the fusion well up on the sides of the crucible and cool it rapidly by dipping it in

cold water, taking care not to let any water get inside of the crucible. When cool, place the crucible and contents in a porcelain dish, add about 100 cubic centimeters of water, and boil to dissolve the fused mass. When the fusion is loosened from the crucible, remove it, and wash it off into the dish by means of a wash bottle. If any hard lumps remain in the solution, they may be broken up by gently rubbing with a pestle, which must afterwards be washed off into the dish.

When the fusion is completely disintegrated, allow the undissolved portion of iron, etc. to settle, and, if the solution has a green or red tint, add a few drops of alcohol to precipitate the manganese, which causes this color. Filter, and wash the precipitate thoroughly with hot water, collecting the filtrate and washings in a porcelain dish. Render the filtrate distinctly acid by the cautious addition of concentrate hydrochloric acid, evaporate to dryness, and ignite gently to render the silica insoluble. Moisten the residue with 5 cubic centimeters of concentrate hydrochloric acid, add from 50 to 75 cubic centimeters of water, and heat until the sodium salts are completely dissolved. Filter, and wash thoroughly with hot water, bringing the volume of the filtrate to about 150 cubic centimeters. Heat this filtrate to boiling, add 10 cubic centimeters of a 10-per-cent. solution of barium chloride (or 20 cubic centimeters of a 5-per-cent. solution), and continue the boiling for several minutes.

Stand the solution in a warm place for from 4 to 6 hours for the precipitate to collect and settle in a coarse granular form, filter, wash thoroughly with hot water, and dry in an air bath. Remove the precipitate as completely as possible from the filter and burn the latter in a weighed crucible. Moisten the ash with a drop of nitric and a drop of sulphuric acid, heat gently at first, and then raise the temperature to faint redness to drive off the excess of acid. Add the precipitate, heat to dull redness for 5 minutes, cool in a desiccator, and weigh as barium sulphate $BaSO_4$, which contains 13.73 per cent. of sulphur.

If preferred, the barium sulphate may be filtered on a Gooch felt, but, when this method is employed, the precipitate

is generally obtained in a form so coarse that it does not run through a filter, and, consequently, the use of a Gooch crucible is not necessary. It is frequently advised to heat the barium chloride, used to precipitate the sulphur, to boiling before adding it, in order to obtain the precipitate in a coarser form; but if the boiling is continued for some minutes after the addition of the barium chloride, this is unnecessary.

MANGANESE.

23. More or less manganese is found in nearly all iron ores, and its determination is often a matter of importance. The two methods that are probably the most used are Volhard's method and Ford's method. Both these methods have been more or less modified by different chemists, and they are given here, not exactly as they were originally described by their authors, but as they are most frequently used in practical work.

Volhard's method is quite rapid and simple, and it is the writer's experience that it yields accurate results in all cases. Many chemists, however, do not consider it accurate for ores containing less than .5 per cent. of manganese, and Ford's method is generally considered the more reliable of the two. Hence, although it is longer, Ford's method is generally used when exact results are required, especially if the ore contains but little manganese. Both these methods may be used for manganese ores as well as for the ores of iron.

24. Volhard's Method.—Weigh 1.5 grams of the sample into a porcelain dish, add 20 cubic centimeters of concentrate hydrochloric acid, about 10 drops of concentrate nitric acid, and 15 cubic centimeters of dilute sulphuric acid (1 part of acid of 1.84 Sp. Gr. to 2 parts of water). Evaporate to dryness on a hot plate, and ignite till dense white fumes of sulphur trioxide are given off. When cool, add about 75 cubic centimeters of water, and boil until the sulphates are completely dissolved. Wash the solution into a 300-cubic-centimeter graduated flask, add a strong solution of sodium

carbonate until the solution is almost neutral and assumes a red color, but no precipitate forms; then add an emulsion of zinc oxide in water until the color becomes light brown, generally described as the color of coffee with cream.

Dilute exactly to the mark with pure water, and mix thoroughly. Pour this mixture on a large, dry, fluted filter, placed in a dry funnel, and receive the filtrate in a dry clean beaker. By means of a pipette, transfer 200 cubic centimeters of this filtrate, which represents 1 gram of ore, to a flask, add 1 drop of concentrate nitric acid, and heat it to boiling. As soon as the solution commences to boil, remove it from the source of heat, run in a little standard potassium-permanganate solution, give the flask a sharp rotary motion to cause the precipitate to collect, allow it to partly settle and note the color of the solution. If the solution is colorless, add more permanganate, heat until the solution just commences to boil, shake the flask, allow the precipitate to partially subside, note the color of the solution, and continue this treatment until the supernatant liquid shows a pink color after the precipitate has settled.

When a potassium-permanganate solution is added to a solution of manganese sulphate at about the boiling point, the manganese in both solutions is precipitated according to the equation:

$$2KMnO_4+3MnSO_4+2H_2O = 5MnO_2+2KHSO_4+H_2SO_4$$

When all the manganese in the manganese-sulphate solution is precipitated, the excess of permanganate added gives the solution a pink tint, which indicates the end of the reaction. Knowing the strength of the permanganate solution, the amount of manganese in the sample is readily calculated from the above equation. If the ore contains a very high percentage of manganese, it is best to dilute the 200 cubic centimeters of solution, withdrawn after filtering, to some exact volume, depending on the amount of manganese present; and then take 200 cubic centimeters of this solution for titration.

25. Ford's Method.—Weigh 1 gram of ore into a porcelain dish, add 25 cubic centimeters of concentrate hydrochloric acid and evaporate to complete dryness, but avoid a temperature much above 100°. Add 5 cubic centimeters of concentrate hydrochloric acid and 20 cubic centimeters of water to the residue, and boil till the chlorides are all in solution. Filter off the silica, wash it thoroughly with hot water, and evaporate the filtrate to dryness, but avoid ignition. Dissolve the residue in concentrate nitric acid, and boil the solution down until it is almost syrupy, to expel hydrochloric acid. Add 50 cubic centimeters of concentrate nitric acid, boil for a few minutes, and then add, a little at a time, from 5 to 8 grams of potassium chlorate to oxidize the manganese and precipitate it as manganese dioxide MnO_2. When enough has been added to oxidize the manganese, the greenish-yellow vapors above the solution will give a puff and disappear. Now add about 1 gram more of potassium chlorate and boil about 2 minutes; then cool rapidly by standing the beaker in cold water, and, when it is cold and the precipitate has settled, filter through an asbestos filter.

FIG. 5.

To make a filter for this purpose, bend one end of a stout platinum wire into a rather closely coiled spiral, and insert this in a filtering tube fitted in a filtering flask, as shown in Fig. 5. Pour the asbestos suspended in water into the tube, and, by means of the pump, draw the water through, depositing the asbestos on the spiral, forming a filter, or "plug," as it is generally called. If a wire for this purpose is not at hand, an irregular piece of glass, or a piece of pumice stone that will hold the asbestos in place and permit the free passage of liquid, may be placed in the neck of the filtering tube, and the asbestos deposited on it.

Wash the beaker and precipitate twice with concentrate nitric acid by pouring 15 or 20 cubic centimeters of it into the beaker in which the precipitation was accomplished, and, after running it around in the beaker, pour it on the precipitate and draw it through the plug. When all has passed through the filter, repeat the operation. The acid used for washing the precipitate must be pure and colorless; if it is colored by nitrous fumes, which are always developed in nitric acid that is allowed to stand in the light, it will dissolve the manganese dioxide; but acid thus colored may be purified by passing a current of air through it.

By pressing on the end of the platinum wire extending through the bottom of the filtering tube, force the precipitate and asbestos out into the beaker in which the precipitation was made; or, if a platinum wire were not used, the precipitate and plug may be forced out by means of a thin stirring rod. Add about 30 cubic centimeters of strong sulphurous acid (made by leading sulphur dioxide into water) and 5 cubic centimeters of hydrochloric acid, pouring the acids through the filtering tube to dissolve any precipitate that may be adhering to it. Stir the precipitate and asbestos up with a glass rod, and the acid mixture will rapidly dissolve the manganese dioxide. Filter to remove the asbestos, and wash it well on the filter with hot water. Boil the filtrate until the excess of sulphur dioxide is driven off, add a few drops of concentrate nitric acid, and, after boiling a few moments longer, add a slight excess of ammonium hydrate to precipitate the iron present. Filter, wash several times with hot water, and stand the filtrate aside. Dissolve the precipitate on the filter with hydrochloric acid, allow the solution to run through and wash the filter well with hot water, receiving the solution and washings in a clean beaker. Heat the solution to boiling, reprecipitate the iron with ammonia, filter, and wash the precipitate thoroughly with hot water.

Unite the two filtrates, which will now contain all the manganese freed from other metals, and the volume of which should amount to about 300 cubic centimeters. Add a rather

large excess of microcosmic-salt solution (from 20 to 50 cubic centimeters, according to the amount of manganese present) and dissolve the precipitate thus formed in the least necessary quantity of concentrate hydrochloric acid. Heat the solution to boiling, and, while keeping it as near as possible to the boiling point, add concentrate ammonia, drop by drop, until the last drop causes a permanent precipitate. Now stop the addition of ammonia, and stir the solution vigorously until the precipitate assumes a silky crystalline appearance; then add another drop or two, stir again, and continue this treatment until the manganese is all precipitated in the crystalline condition. Then add 2 or 3 cubic centimeters of the ammonia in excess, and stir well. Stand the beaker in a cool place until the solution is cool and the precipitate has completely settled.

It may be filtered after standing 20 minutes, but if there is no hurry, it is best to allow it to stand 2 hours. Filter and wash thoroughly, but not excessively, with water made slightly alkaline with ammonia, and containing 100 grams of ammonium nitrate to the liter. Dry in an air bath, remove the precipitate as completely as possible from the filter, and burn the latter in a weighed crucible. Add the precipitate, ignite intensely over the blast lamp, cool in a desiccator, and weigh as manganese pyrophosphate $Mn_2P_2O_7$, which contains 38.73 per cent. of manganese.

SOLUTIONS FOR MANGANESE DETERMINATIONS.

26. Zinc Oxide.—The zinc-oxide emulsion, used to precipitate the iron in Volhard's method, is prepared by mixing pure zinc oxide with water until it has a creamy consistency. The zinc oxide separates out on standing, and, consequently, it must be shaken thoroughly before it is used.

27. Potassium Permanganate.—The standard permanganate solution, used in titrating iron, may be used for this determination by making a calculation. The manganese is precipitated according to the equation:

$$2KMnO_4 + 3MnSO_4 + 2H_2O = 5MnO_2 + 2KHSO_4 + H_2SO_4$$

Hence we see that 2 molecules of permanganate, which oxidize 10 molecules of ferrous sulphate, only oxidize 3 molecules of manganese sulphate. Taking the atomic weights of iron and manganese as 56 and 55, respectively, we have $\frac{55}{56} \times \frac{3}{10} = \frac{33}{112}$, or .2946. That is, the value of the permanganate solution in iron, multiplied by .2946, gives its value in manganese, or the value of a permanganate solution in manganese is 29.46 per cent. of its value in iron.

It is best, however, if many determinations are to be made, to make, for this purpose, a solution of permanganate of such strength that the percentage of manganese may be read directly from the burette, and this plan is universally adopted in iron-works laboratories where this method is used. If the solution titrated represents one gram of ore, the permanganate solution should be made of such strength that 1 cubic centimeter of it oxidizes .001 gram of manganese, corresponding to .1 per cent. The method of standardizing will be readily understood from the above calculation.

PIG IRON.

28. As pig, or cast, iron is the first product in the manufacture of iron and steel, its analysis will be treated next. The principal determinations, and, in fact, the only determinations frequently made, are four in number; viz., *silicon*, *sulphur*, *phosphorus*, and *manganese*. As all these elements tend to segregate to a greater or less extent, pig iron is never homogeneous; a single pig will not have exactly the same composition throughout, and, if samples are taken from different parts of a cast, the variation will be still greater; hence the selection of a sample becomes a matter of importance. If a cast is to be sampled, probably the best method is to remove three samples of the molten iron, as it runs from the furnace, by means of a ladle, taking the first sample soon after the iron begins to run, the second when about half of it has passed out, and the third towards the end of the cast. After these test pieces have cooled, break them, drill an equal amount from the interior of each piece, and mix the drillings.

A sample is thus obtained that, as a rule, quite closely represents the composition of the whole cast.

If a car of metal is to be sampled, pigs should be taken from different parts of the car, then broken, and mixed with the same quantity of drillings taken from the interior of each pig. This method should also be employed in sampling a pile of iron.

Iron drillings are always likely to contain sand and scale, and these must be removed before weighing up a sample. This is best done as follows: Spread the drillings on a clean paper, place another paper over them and bring a magnet in

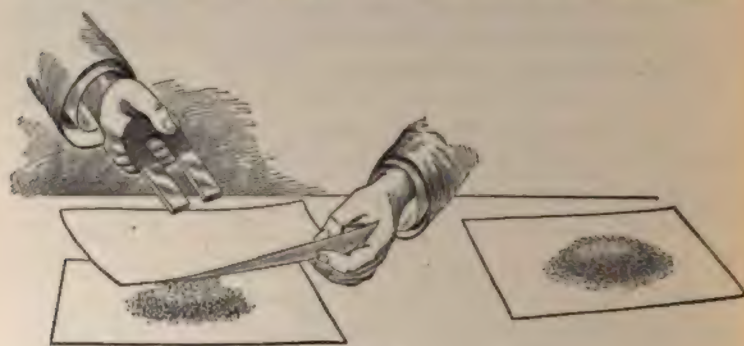


FIG. 6.

contact with this paper. By lifting up on the magnet, which attracts the drillings and holds them close to the paper, remove part of the drillings and hold them over another clean paper. Then by holding the paper between the magnet and drillings firmly, and withdrawing the magnet, allow the drillings to fall on the paper placed to receive them. By repeating this a few times, all the drillings will be removed to the second paper, while the sand and scale, being non-magnetic, will remain on the first. The method of accomplishing this is illustrated in Fig. 6. Now, after mixing the sample thoroughly to get a uniform mixture of coarse and fine drillings, which usually differ somewhat in composition, the sample is ready to be weighed out for the different determinations.

It should be mentioned at this point that a short piece of thick iron wire, ground to a point and magnetized, is very handy in transferring small particles of the sample to and from the weighing glass on the pan of the balance.

SILICON.

29. Drown's Method.—For this determination, the method proposed by Dr. Drown, or a slight modification of the same, is almost universally adopted. The method, as it is probably most frequently employed, is as follows: Weigh 1 gram of drillings into a porcelain dish, cover the dish with a watch glass, and add 20 cubic centimeters of nitric acid of 1.2 Sp. Gr., drawing the glass aside to admit the acid. If the drillings are very fine, the acid should be added cautiously to prevent loss during solution. When violent action ceases, add 15 cubic centimeters of dilute sulphuric acid (1 part of acid to 2 parts of water), evaporate to dryness on a hot plate, or over the bare flame of an Argand burner, and continue to heat until copious white fumes of sulphur trioxide are given off.

If the heat is carefully regulated, the evaporation may be accomplished without spattering, but as there is always more or less danger, it is best to keep the dish covered with a watch glass to catch any particles that may spatter against it, and would otherwise be lost, and to boil the solution down rapidly. When cool, add 15 cubic centimeters of dilute hydrochloric acid (equal parts of acid and water, generally spoken of as 1 : 1 acid), then from 30 to 50 cubic centimeters of water, and boil vigorously until the sulphates are completely dissolved. Wash any precipitate adhering to the watch glass into the solution, and, after allowing it to stand a few moments for the precipitate to settle, filter while still quite warm, preferably with the aid of a filter pump. Wash twice with hot water, then fill the filter with warm dilute hydrochloric acid (generally 1 : 1), and when this has passed through, continue to wash with hot water until the iron is completely removed from the precipitate

and filter. The precipitate now consists of silica and graphite. Wrap the filter around it, place them in a platinum crucible, and, after igniting moderately to burn the paper, heat at the full power of the blast lamp until the graphite is burned off, leaving the precipitate perfectly white. When cool, weigh as silica SiO_2, which contains 47.02 per cent. of silicon.

The results obtained as just directed are accurate enough for all practical purposes, but, if absolute accuracy is required, add 2 or 3 drops of sulphuric acid to the silica after weighing it; then dissolve it in hydrofluoric acid, evaporate to dryness, ignite, cool, and weigh the residue, if any, remaining in the crucible. The difference between the two weights is the weight of silica which has been expelled by heating the hydrofluoric-acid solution. When many determinations are made daily, this method is frequently modified as follows: Weigh .9404 gram of the sample into a porcelain dish, dissolve it in 25 cubic centimeters of mixed acids (made up in the proportion of 18 parts of nitric acid of 1.2 Sp. Gr. to 7 parts of half-strength sulphuric acid), evaporate to dryness, and heat until dense white fumes of sulphur trioxide are given off. When cool, dissolve the sulphates in hydrochloric acid and water, filter, wash, ignite (usually in a muffle furnace), and weigh. As .9404 is twice the factor weight (.4702) of silicon, the weight of silica divided by 2 is the percentage of silicon. When precipitates are ignited in a muffle furnace, they are usually placed, together with the filter, in a platinum crucible that is supported on a tripod of platinum wire, as shown in Fig. 7. The crucible standing in the tripod is placed in a muffle maintained at a white heat until the precipitate is white, then it is removed and is weighed as soon as cool. As twenty-five or thirty precipitates may be ignited at one time in a muffle, much time is saved by this method of ignition if many determinations are being made.

FIG. 7.

SULPHUR.

30. A number of methods for the determination of sulphur in iron have been proposed, but only two, known as the *evolution method* and the *aqua-regia method*, are used very extensively in iron-works laboratories. The evolution method depends on the fact that all the sulphur in iron exists in the form of sulphide, and can ordinarily be evolved in the form of hydrogen sulphide by treating the sample with hydrochloric acid. By the aqua-regia method, the sulphur is oxidized to sulphate, and is precipitated and weighed as barium sulphate.

The evolution method is rapid and simple, and with most samples yields extremely accurate results. Occasionally, however, a sample is met that will not yield all its sulphur by this method; hence, in settling disputes, and in establishing standards, the aqua-regia method should always be employed.

31. The Evolution Method.—Weigh 5 grams of drillings into a flask having a capacity of 750 or 800 cubic centimeters, and close the flask with a doubly perforated stopper. Through one of the perforations of this stopper pass a funnel tube with a stop-cock, reaching nearly to the bottom of the flask, and, through the other, pass a short delivery tube bent at right angles, over the end of which a short piece of rubber tubing is tightly fitted. Place a tight-fitting, doubly perforated rubber stopper in a test tube containing a solution of potassium hydrate, and through one perforation pass a glass tube reaching nearly to the bottom of the test tube, and connect this with the rubber tube attached to the delivery tube of the flask. Through the other perforation pass the short limb of a tube bent twice at right angles, so that it reaches just through the stopper, and pass the longer limb nearly to the bottom of a second test tube, fitted like the first. Each tube should contain about 2 inches of potassium-hydrate solution. Fit the flask in a suitable support over an Argand burner. The test tubes may be supported by the tube connecting them.

The arrangement of the apparatus will be understood from Fig. 8. Close the apparatus, and pour from 90 to 100 cubic centimeters of hydrochloric acid (1 : 1) into the funnel tube. Then turn the stop-cock, allowing the acid to run into the flask, and, as soon as it is all in, close it again. The iron is rapidly dissolved with the evolution of hydrogen, and the sulphur, which is in the form of sulphide, is evolved as hydrogen sulphide. The gases pass through the test tubes containing potassium hydrate where the hydrogen sulphide is absorbed with the formation of potassium sulphide.

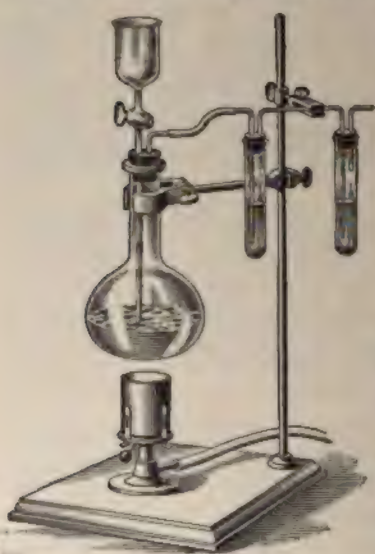


FIG. 8.

When the evolution of gas slackens, light the burner under the flask, and turn it low until the iron is all dissolved; then raise the temperature and boil the solution until all hydrogen sulphide is expelled and the solution in the first test tube is quite warm from the steam passing over from the flask. Now open the stop-cock of the funnel tube, turn out the light, and disconnect the rubber tube connecting the flask and test tubes. Remove the test tubes, pour their contents into a beaker, and thoroughly wash the test tubes and tubes leading into them, allowing the washings to run into the solution in the beaker, which is then diluted to about 300 cubic centimeters. Add about 5 cubic centimeters of starch solution, render the solution distinctly acid with hydrochloric acid, and titrate at once with a standard solution of iodine.

When the solution is rendered acid with hydrochloric acid, hydrogen sulphide is formed, and this reacts with the iodine according to the equation:

$$H_2S + I_2 = 2HI + S$$

This reaction takes place as long as the solution contains hydrogen sulphide, but as soon as this is consumed, the iodine commences to unite with the starch, forming blue starch iodine; hence the appearance of a permanent blue color indicates the end of the reaction. The solution must be titrated immediately after it is acidified, or the hydrogen sulphide formed will partly escape, and the results obtained will be too low. For the same reason, the acid used to acidify the solution should be added quickly.

In iron-works laboratories, a series of supports is generally arranged over stationary Argand burners, which are much better than Bunsen burners for this purpose; but for practice, or for an occasional determination, the apparatus shown in Fig. 8 serves very well, and in such cases a Bunsen burner or even an alcohol lamp may be substituted for the Argand burner.

32. The Aqua-Regia Method.—Weigh 5 grams of drillings into a porcelain dish, or, still better, a porcelain beaker, and quickly add 50 cubic centimeters of nitric acid of 1.42 Sp. Gr., so that the sample is completely covered at once. If rapid solution commences at once, stand the porcelain dish in cold water to check the action. If the sample does not begin to dissolve in a few moments, add a few drops of concentrate hydrochloric acid, and heat it gently. Violent action may be checked by standing the dish in cold water, preferably, ice water.

About 10 cubic centimeters of hydrochloric acid should be added in small portions during the solution. When this is all in, and the sample is dissolved, add about ½ gram of potassium chlorate and 1 gram of sodium carbonate, evaporate to dryness, and ignite slightly. Dissolve the residue in 20 or 25 cubic centimeters of concentrate hydrochloric acid, evaporate to dryness, and again ignite gently to render the silica insoluble. Dissolve the residue in 25 or 30 cubic centimeters of concentrate hydrochloric acid, and evaporate until the solution becomes syrupy; then add 5 cubic centimeters more of concentrate hydrochloric acid, and heat

gently till the solution becomes clear. Dilute this solution with a little more than twice its own volume of hot water, mix thoroughly, filter through a paper that has previously been washed with hot dilute hydrochloric acid, and wash the filter thoroughly with hot water, adding a few drops of hydrochloric acid, if necessary, to remove red stains from the paper.

Heat the filtrate, which should amount to about 200 cubic centimeters, to boiling, add 20 cubic centimeters of a 5-per-cent. solution of barium chloride, or 10 cubic centimeters of a 10-per-cent. solution, and continue the boiling a few minutes. Stand the solution in a warm place for at least 2 hours; then filter, and wash thoroughly on the filter with hot water, acidulated with a few drops of hydrochloric acid. Dry the precipitate in an air bath, remove it as completely as possible from the filter, and burn the latter in a weighed crucible. Add 1 or 2 drops each of concentrate nitric and sulphuric acids, evaporate to dryness, and ignite gently to expel the excess of acid. When cool, add the precipitate, heat to dull redness, cool in a desiccator, and weigh as barium sulphate $BaSO_4$, which contains 13.73 per cent of sulphur.

A Gooch crucible may be used instead of a filter paper in filtering the barium sulphate, and is preferred by many chemists on account of the tendency of the precipitate to pass through a filter, and the ease with which it is reduced when ignited in the presence of carbonaceous matter.

In the case of some samples of iron containing a high percentage of sulphur, a small quantity of this element appears to escape oxidation when the sample is dissolved as above directed. In such cases, it is best to stand the dish containing the sample in cold water, add the nitric acid quickly so that the drillings are entirely covered at once, and allow the dish to stand in the cold water about an hour. Then add 10 cubic centimeters of concentrate hydrochloric acid, and allow the dish to stand in a cool place several hours longer before applying heat to effect solution. In this way, much of the sulphur is oxidized before there is

any apparent action, and the results obtained are slightly higher, in some cases, than when the sample is dissolved in the usual manner.

SOLUTIONS FOR SULPHUR DETERMINATIONS.

33. Potassium Hydrate.—The potassium-hydrate solution used to absorb the hydrogen sulphide is made of different strengths by different chemists. A very good solution is made by dissolving 1 part of potassium hydrate in about 5 parts of water. In practical work, this solution is generally made as follows: Place 1 pound of pure potassium hydrate in a 5-pound ($2\frac{1}{2}$-liter) bottle, fill the bottle to about two-thirds its capacity with water, and stir gently from time to time until all is dissolved; then fill the bottle with water and mix the contents thoroughly. When cool, the solution is ready for use. Many chemists use a more dilute solution for this purpose, but when potassium hydrate is used, a solution of about the strength given above is usually employed.

The potassium-hydrate solution has a number of advantages, but, as a matter of economy, an ammoniacal solution of cadmium chloride is largely used in its stead at present. This solution is made up as follows: Dissolve 100 grams of cadmium chloride in 500 cubic centimeters of water and 500 cubic centimeters of concentrate ammonia, and filter through a fluted filter into a large bottle. To the filtrate add 2 liters of concentrate ammonia and 2 liters of water, and mix thoroughly. When this solution is employed for the absorption, a single test tube 1 inch in diameter and 10 or 12 inches in length, with a delivery tube reaching to the bottom, is generally used. About 25 cubic centimeters of the cadmium solution, diluted to about 100 cubic centimeters, are introduced into the tube, and the determination proceeded with as directed. It is safer, however, to divide this solution between two test tubes, as is done when potassium hydrate is employed, though larger tubes should be used in this case.

34. Starch Solution.—To make the starch solution for the indicator, mix from 5 to 10 grams of pure starch with

40 or 50 cubic centimeters of water; pour this into a liter of boiling water, and continue the boiling a few moments, meanwhile stirring with a glass rod. Allow the solution to settle, and decant the clear liquid for use. A fresh solution should be made up at least once a week.

35. Standard Iodine Solution.—The iodine solution is made of such strength that 1 cubic centimeter represents .0005 gram of sulphur, or .01 per cent. of sulphur when 5 grams of sample are taken. The reaction between hydrogen sulphide and iodine is

$$H_2S + I_2 = 2HI + S$$

or 253 grams of iodine set free 32 grams of sulphur. Hence, in order that 1 cubic centimeter of the solution shall represent .0005 gram of sulphur, 1 liter of it must contain 3.953 grams of iodine.

It is probably best to standardize the iodine solution against a steel of known sulphur content. This is done as follows: Dissolve 10 or 12 grams of potassium iodide in from 50 to 75 cubic centimeters of cold water, add 4 grams of freshly sublimed iodine, stir till all is dissolved, and dilute to about 1 liter. Then dissolve 5 grams of the standard steel in half-strength hydrochloric acid, absorb the hydrogen sulphide in potassium hydrate, as directed in Art. **31**, and titrate with this solution. From the result thus obtained, calculate how much the solution must be diluted, add the calculated amount of water and mix thoroughly. Then make another determination, using the standard steel, to be sure that the solution is right. This solution should be kept in a dark, cool place and should be restandardized once a week.

As potassium bichromate liberates iodine from its compounds, an iodine solution may be made up and standardized at the same time by the use of a standard solution of potassium bichromate. The reaction is as follows:

$$K_2Cr_2O_7 + 6KI + 14HCl = 8KCl + 2CrCl_3 + 7H_2O + 3I_2$$

Hence, 1 cubic centimeter of a decinormal solution of

potassium bichromate, which oxidizes .0056 gram of iron, liberates .01265 gram of iodine, and 312.5 cubic centimeters liberate 3.953 grams of iodine. The solution is made up as follows:

Dissolve about 15 grams of potassium iodide in 200 cubic centimeters of water. Then dilute 10 cubic centimeters of concentrate hydrochloric acid to 200 cubic centimeters, add this to the potassium-iodide solution, and, from a burette, run in 312.5 cubic centimeters of decinormal bichromate solution while stirring continuously. Dilute this solution to exactly 1 liter and mix it thoroughly, when it will be ready for use.

The same volume of a decinormal solution of potassium permanganate may be used instead of the bichromate by substituting sulphuric for hydrochloric acid. If this is done, pour 10 cubic centimeters of concentrate sulphuric acid into 200 cubic centimeters of water, and, after this solution has cooled, slowly pour it into the potassium-iodide solution while stirring continuously. Add 312.5 cubic centimeters of decinormal permanganate solution to this, and proceed as with the bichromate. The reaction in this case is as follows:

$$2KMnO_4 + 10KI + 8H_2SO_4$$
$$= 6K_2SO_4 + 2MnSO_4 + 8H_2O + 5I_2$$

PHOSPHORUS.

36. A number of methods for the determination of phosphorus in pig iron are in general use. In most of these methods, the phosphorus is first precipitated as ammonium phospho-molybdate, generally spoken of as "yellow precipitate," and the various methods differ principally in the treatment of the yellow precipitate.

37. Obtaining the Yellow Precipitate.—Weigh 5 grams of the drillings into a porcelain dish, cover with a watch glass, and add 70 cubic centimeters of nitric acid of 1.2 Sp. Gr. When violent action ceases, place the dish on a tripod over an Argand burner, which is turned very low

until solution is complete. This will usually require about half an hour. Now raise the temperature, evaporating to dryness as rapidly as possible, and ignite the residue until acid fumes are no longer given off. The carbonaceous matter is thus destroyed, and the phosphorus is oxidized to phosphate. When cool, add 35 cubic centimeters of concentrate hydrochloric acid and heat gently till the residue is dissolved; then raise the temperature, and evaporate as rapidly as possible, with the cover on, until the solution becomes syrupy, thus expelling as much hydrochloric acid as possible without having iron salts separate.

Remove the dish from the burner, and immediately add 7 cubic centimeters of concentrate nitric acid; then, without delay, wash any iron solution adhering to the watch glass and the sides of the dish down into the main solution, using from 75 to 100 cubic centimeters of warm water, and stir the solution well. Filter into a flask having a capacity of about 700 cubic centimeters, and wash the filter and residue thoroughly with a 2-per-cent. solution of nitric acid. To the solution in the flask add 30 cubic centimeters of concentrate ammonia, shake the flask until the precipitate becomes smooth, and then add enough concentrate nitric acid to dissolve it, forming a clear amber-colored solution. About 32 cubic centimeters will generally be the right amount of acid.

Suspend a thermometer in the solution, bring its temperature to exactly 85°, add 75 cubic centimeters of ammonium molybdate, and agitate the contents of the flask for 5 minutes by giving the flask a rotary motion, or by shaking it. The phosphorus will now be completely precipitated as ammonium phospho-molybdate. After allowing it to settle for 15 or 20 minutes, filter and determine the phosphorus in it by one of the following methods.

38. Weighing as Magnesium Pyrophosphate.—Wash the yellow precipitate thoroughly with 2-per-cent. nitric acid, dissolve it in ammonia, precipitate the phosphorus as magnesium-ammonium phosphate, ignite strongly, and weigh as

magnesium pyrophosphate, following the directions given in Art. **16**.

This method is much longer than some of the others, but, as it is probably the most reliable of any, it is largely used in settling disputes, and in other cases where extreme accuracy is required.

39. Titration With Permanganate.—Wash the precipitate thoroughly with an acid ammonium-sulphate solution, place the funnel in the neck of a 500-cubic-centimeter flask, spread the filter on the side of the funnel, or break its apex with a glass rod, and wash as much of the precipitate as convenient into the flask with water. To dissolve the precipitate adhering to the paper, pour dilute ammonia over it, and wash the paper thoroughly with water, allowing all the solution to run into the flask.

Enough ammonia should be added to dissolve all the yellow precipitate, both on the filter and in the flask, but a large excess should be avoided. Pour 15 grams of granulated zinc into the flask, add 100 cubic centimeters of dilute sulphuric acid (made by adding 1 part of concentrate acid to 3 parts of water), place a small funnel in the neck of the flask and heat gently for half an hour, when reduction will be complete.

Pour the contents of the flask, which should still contain some undissolved zinc, upon a large folded filter, receiving the filtrate in a large beaker. Rinse out the flask with water, and, as soon as the main solution has passed through, pour this on the paper. When these washings have passed through, fill the filter once with cold water, and, as soon as this passes through, titrate the solution with potassium permanganate.

As the permanganate is added to the solution, it gradually changes color, and finally becomes colorless. A few additional drops of the permanganate will now impart a faint pink to the solution, indicating that the reaction is complete. From the amount of permanganate used, the percentage of phosphorus in the sample is obtained.

40. Titration With Nitric Acid.—Wash the yellow precipitate four times with a 2-per-cent. solution of nitric acid, and then four times with a 1-per-cent. solution of potassium nitrate. Remove the filter containing the yellow precipitate to a beaker, add standard sodium-hydrate solution in sufficient quantity to completely dissolve the precipitate, and stir with a glass rod until the filter paper is broken up into a pulp. About 30 cubic centimeters of the standard sodium hydrate will usually be sufficient. It should be added from a burette, and the amount used should be carefully noted. Dilute the solution to 75 or 100 cubic centimeters with water, add a few drops of phenol-phthalein, and titrate with a standard solution of nitric acid that exactly matches the standard sodium hydrate. The quantity of sodium hydrate used to dissolve the precipitate, minus the amount of nitric acid required to neutralize the excess of sodium hydrate, gives the amount of sodium hydrate actually needed to dissolve the precipitate, and, from this, the percentage of phosphorus is calculated.

41. Weighing the Yellow Precipitate.—As ammonium phospho-molybdate, precipitated as above directed, contains 1.63 per cent. of phosphorus, it may be weighed, and the phosphorus thus determined. If this method is employed, filter through a paper that has been dried at 110° in an air bath for 1 hour, and weighed quickly between matched glasses. Wash the precipitate from six to ten times with a 2-per-cent. solution of nitric acid, place the filter containing the precipitate on a piece of porcelain in an air bath, dry for 1 hour at 110°, and weigh quickly between matched glasses. The increase over the first weight is the weight of the yellow precipitate, and as this contains 1.63 per cent. of phosphorus, the percentage of phosphorus in the sample is readily calculated from this weight.

SOLUTIONS FOR PHOSPHORUS DETERMINATIONS.

42. Acid Ammonium Sulphate.—To make up the acid ammonium-sulphate solution used in washing the yellow precipitate, add 27 cubic centimeters of concentrate ammonia

to ½ liter of water; then slowly add 25 cubic centimeters of concentrate sulphuric acid, and dilute the solution to 1 liter with cold water. After mixing the solution well, and allowing it to cool, it is ready for use.

43. Standard Potassium Permanganate.—When the yellow precipitate is acted on by nascent hydrogen, generated by the zinc and sulphuric acid, the molybdic oxide is reduced to a lower oxide, the exact composition of which is still in doubt, but which appears to be $Mo_{12}O_{19}$. When permanganate is added to this, the molybdenum is oxidized to molybdic oxide again, probably according to the equation:

$$5Mo_{12}O_{19}+34KMnO_4 = 60MoO_3+17K_2O+34MnO$$

At all events, 34 molecules of $KMnO_4$ produce 60 molecules of MoO_3. From this we see that 2 molecules of permanganate, which oxidize 560 parts of iron, will produce 508.23 parts of MoO_3 from the reduced oxide; or, the strength of a permanganate solution in terms of molybdic oxide is 90.76 per cent. of its strength in terms of iron. As the yellow precipitate contains 1.794 per cent. as much phosphorus as molybdic oxide, the strength of the permanganate solution in terms of phosphorus is 1.628 per cent. of its strength against iron. From this the percentage of phosphorus may readily be calculated when the titration is performed with any permanganate solution of known strength. In practical work, however, it is much more convenient to make a permanganate solution of such strength that 1 cubic centimeter = .006141 gram of iron. Its strength against molybdic oxide is 90.76 per cent. of this, or .005574 gram, and its strength against phosphorus is 1.794 per cent. of this, or .0001 gram.

To make such a solution, dissolve .8597 gram of ferrous ammonium sulphate, which contains .12282 gram of iron, in 150 cubic centimeters of water and 15 cubic centimeters of concentrate sulphuric acid, titrate with the permanganate, and dilute until just 20 cubic centimeters are required to oxidize the iron in this quantity of ferrous ammonium

sulphate. To make the permanganate solution, dissolve 3.5 grams of pure potassium permanganate in water, dilute to a little less than 1 liter, and let it stand in a cool dark place 2 or 3 days before the first titration. When this is diluted until 20 cubic centimeters of it just oxidize .12282 gram of iron, 1 cubic centimeter of it represents .0001 gram of phosphorus. After standardizing the solution in this way, it is best to test it against a standard steel or iron in which the phosphorus has been repeatedly determined gravimetrically, by weighing as magnesium pyrophosphate.

44. Sodium Hydrate and Nitric Acid.—These solutions are usually made up of a convenient strength and made to match each other exactly, and the factor for phosphorus is then calculated. In laboratories where large quantities of these solutions are used, this is usually done as follows: Dissolve 77 grams of sodium hydrate in 500 cubic centimeters of water, and to this add a saturated solution of barium hydrate, drop by drop, as long as a precipitate forms; then filter at once, dilute the solution to 1 liter, mix thoroughly, and keep in a tightly stoppered bottle as a stock solution. For use, dilute 200 cubic centimeters of the stock solution to 2 liters, mix thoroughly, and standardize against the nitric-acid solution made up as follows:

Dilute 100 cubic centimeters of nitric acid of 1.42 Sp. Gr. to 1 liter, mix thoroughly, and keep in a tightly stoppered bottle as a stock solution. A solution of approximately the right strength for use is made by diluting 200 cubic centimeters of this stock solution to 2 liters and mixing thoroughly.

Having now the two solutions of approximately the right strength for use, the next step is to standardize them so that they exactly match each other. To do this, measure 25 cubic centimeters of the sodium hydrate into a beaker from a burette, add about 50 cubic centimeters of water, and a few drops of phenol-phthalein; titrate with the nitric acid, and dilute the stronger solution until 25 cubic centimeters of one exactly neutralize 25 cubic centimeters of the other.

The method of calculating the factor for phosphorus is best explained by means of an example. Weigh .3 gram of pure ammonium phospho-molybdate into a beaker, and, from a burette, add standard sodium hydrate in sufficient quantity to completely dissolve it. Let us suppose that 30 cubic centimeters of the solution are added. Dilute this with about 50 cubic centimeters of water, add a few drops of phenol-phthalein, and titrate with the standard nitric acid. If 6 cubic centimeters of this are used in neutralizing the excess of sodium hydrate in the solution, it shows that 24 cubic centimeters of the standard sodium hydrate were actually used in dissolving .3 gram of the yellow precipitate. As the yellow precipitate contains 1.63 per cent. of phosphorus, 1 gram of it contains .0163 gram of phosphorus, and .3 gram of it contains .00489 gram. Hence, 24 cubic centimeters of the sodium hydrate = .00489 gram, and 1 cubic centimeter = .000204 gram of phosphorus.

The number of cubic centimeters of sodium hydrate actually used to dissolve the precipitate, multiplied by this factor, gives the weight of phosphorus, and this, divided by the weight of sample taken, and the result multiplied by 100, gives the percentage of phosphorus in the sample. In practical work, however, it is handier to drop the first two ciphers in the factor instead of multiplying the result by 100.

MANGANESE.

45. The three methods most frequently used for the determination of manganese in iron are Ford's method, Volhard's method, and the color method. Ford's method is regarded as the most reliable, and is very largely used in settling disputes, establishing standards, etc., but it is too long to be very largely used in doing the routine work of an iron-works laboratory. Volhard's method, if properly carried out, yields very accurate results, and is sufficiently short to be largely employed in routine work. The color method is not generally considered as reliable as the other methods in the case of iron, but, on account of the rapidity with which

it yields results, it is quite largely used as a guide in manufacturing processes, and, in the hands of an experienced chemist, it yields very satisfactory results.

46. Ford's Method.—Dissolve 5 grams of the drillings in 65 cubic centimeters of nitric acid of 1.2 Sp. Gr., and boil until the solution becomes almost syrupy; then add 100 cubic centimeters of nitric acid of 1.42 Sp. Gr., boil for a few moments, and add from 5 to 10 grams of potassium chlorate to the boiling solution, a little at a time, to precipitate the manganese as dioxide. When precipitation is complete, the greenish-yellow gas above the liquid gives a puff and disappears. Now add 1 gram more of potassium chlorate, boil 1 or 2 minutes, and cool rapidly by standing the beaker in cold water. When the solution has become cold and the precipitate has settled, filter through asbestos, and from this point proceed as directed in Art. **25.**

47. Volhard's Method.—Dissolve 1.5 grams of the drillings in a porcelain dish in 25 cubic centimeters of nitric acid of 1.2 Sp. Gr., and when the violent action ceases, add 12 cubic centimeters of half-strength sulphuric acid; evaporate to dryness, and ignite until dense white fumes of SO_3 are given off. Allow the residue to cool, add 100 cubic centimeters of water, and boil until solution is complete. When cool, wash the solution into a 300-cubic-centimeter graduated flask, nearly neutralize the acid with a concentrate solution of sodium carbonate, and add an emulsion of zinc oxide in water until the mixture assumes the color of coffee with cream. Dilute with water to exactly 300 cubic centimeters, mix thoroughly, and pour the solution through a large fluted filter placed in a dry funnel, receiving the filtrate in a clean dry beaker. By means of a pipette, transfer 200 cubic centimeters of this solution to a 500-cubic-centimeter flask, add 1 drop of concentrate nitric acid, heat to boiling, and titrate with potassium permanganate, bringing the solution just to boiling, and shaking it well after each addition of permanganate, to cause the precipitate formed to collect and settle

rapidly. A pink tinge in the clear liquid above the precipitate indicates the end of the reaction.

48. The Color Method.—Weigh out .2 gram of standard iron in which the manganese has been carefully determined, and pour it into a 10-inch test tube; then place exactly the same weight of the sample to be tested in a similar test tube, and dissolve each in 25 cubic centimeters of nitric acid of 1.2 Sp. Gr. When violent action ceases, stand the tubes on a sand bath heated by a good burner, or suspend them over Argand burners, and, after solution is complete, boil them gently until the yellowish fumes are entirely expelled from the tubes. Then add about 2 grams of lead peroxide to each and continue the boiling for 3 minutes. The lead peroxide oxidizes the manganese to permanganic acid, which has the well known color of potassium permanganate. Cool the solutions rapidly by standing the test tubes in cold water.

When the solutions are cool, and the insoluble matter has completely settled, decant the standard into a graduated reading tube having an inside diameter of about ½ inch, and dilute it until each cubic centimeter of the solution represents .01 per cent. of manganese. For example, if the standard iron contains .3 per cent. of manganese, dilute the solution to 30 cubic centimeters. Then decant the solution to be tested into a similar reading tube, and dilute it until it has exactly the same color as the standard. Each cubic centimeter of this solution will then represent .01 per cent. of manganese; thus, if the solution is diluted to 35 cubic centimeters to make the colors agree, the sample contains .35 per cent. of manganese. If care is taken in decanting the solutions from the test tubes to the reading tubes, all but 2 or 3 drops of the liquid may be decanted without introducing any of the insoluble matter.

Instead of heating the samples over a burner or on a sand bath, the tubes are sometimes stood in a solution of calcium chloride that boils at 115°. In this way, the solutions may be boiled without danger of breaking the tubes. It is scarcely

necessary to add, that, in order to obtain correct results, the standard and the sample to be tested must be treated in as near the same manner as possible.

CARBON.

49. Carbon is not usually determined in pig iron, but occasionally the percentage of this element is required. When this is the case, it is determined by one of the combustion methods given in Art. **55** *et seq.*, using 1 gram of the sample and a corresponding amount of solvent. The color method for carbon is not applicable in the case of pig iron.

STEEL.

50. Although steel is usually more regular than pig iron in composition, it is still far from homogeneous in many instances, and, consequently, in taking a sample, drillings from different parts of the piece sampled should be obtained if possible. The bottom of an ingot seldom has exactly the same composition as the top, and the center of a rod or wire usually differs in composition from the metal at the surface. These irregularities in composition should always be taken into account when selecting a sample for analysis. A sample of steel is not so likely to contain sand as is pig iron, but it may contain scale, and, if this is present, the sample should be freed from it by means of the magnet, as in the case of pig iron.

The principal determinations made in the analysis of steel are *silicon*, *sulphur*, *phosphorus*, *manganese*, and *carbon*. Silicon is less frequently determined than the other elements, but its estimation is important in some cases. Sulphur and manganese are determined in steel in exactly the same way that they are estimated in iron, and, as the determination of these elements in pig iron has been thoroughly described, they will not be treated at this point. It should be stated, however, that the color method for manganese is considered more reliable in the case of steel than when

applied to pig iron. In fact, for the routine work in steel-works laboratories, it is used much more than any other method.

It is frequently stated that the color method is only accurate for samples containing less than 1 per cent. of manganese, but chemists that have used this method largely, usually regard it as reliable in the case of all samples containing less than 2 per cent., and some experiments seem to show that it will yield satisfactory results with samples containing even higher percentages. A standard steel, having, approximately, the same percentage of manganese as the sample tested, should always be used; hence, it is best to have several standards containing different quantities of manganese. Sometimes samples of iron are compared with a steel standard, but, as a rule, it is best to compare samples of steel with a steel standard, and samples of iron with an iron standard. Aside from what has just been said, in determining sulphur and manganese in steel, the directions given for the determination of these elements in iron should be followed exactly.

SILICON.

51. Weigh 5 grams of the drillings into a porcelain dish, cover it with a watch glass, add 50 cubic centimeters of nitric acid of 1.2 Sp. Gr., and 35 cubic centimeters of half-strength sulphuric acid, and evaporate rapidly over an Argand burner until the solution begins to bump; then turn out the flame, remove the cover, and stir the syrupy solution vigorously for a few moments, when it will solidify. Or, after adding the acid, stand the dish on a sand bath, with the cover drawn to one side, and allow it to slowly evaporate to dryness. In either case, heat the residue over an Argand burner until dense white fumes are given off. When cool, add 30 cubic centimeters of half-strength hydrochloric acid and about 75 cubic centimeters of water; heat until solution is complete, and boil the solution a few minutes to make sure that all iron salts are dissolved. Filter through a small ashless filter, wash first with half-strength hydrochloric

acid, then once with water, then again with half-strength hydrochloric acid, and, finally, wash five or six times with water. Wrap the filter around the precipitate, place them in a platinum crucible, and, after burning off the paper, ignite intensely over a blast lamp. Cool in a desiccator and weigh as silica SiO_2, which contains 47.02 per cent. of silicon.

Sometimes a correction is made as follows: Dissolve the precipitate of SiO_2 in hydrofluoric acid, add 2 or 3 drops of sulphuric acid, evaporate to dryness, ignite, cool, and weigh again. If the determination is properly performed, this is unnecessary, for, in this case, the result obtained by the correction will seldom, if ever, differ from the first result; and, if there is a difference, it will be very slight.

PHOSPHORUS.

52. The phosphorus in steel may be determined by any of the methods described for the determination of this element in iron, and one of these methods is generally employed. In addition to these, however, Dr. Drown has proposed a method in which the phosphorus is oxidized and the organic matter destroyed by potassium permanganate in a nitric-acid solution, and, on account of its rapidity, this method is quite largely employed. Other methods of oxidizing the phosphorus in solution have also been proposed, but none of these have come to be used so generally as that proposed by Dr. Drown. It has been stated that some samples of steel—notably, those containing a high percentage of carbon—do not yield all their phosphorus when oxidized by any of these wet methods, but this objection does not appear to be proven. Dr. Drown's method yields very accurate results with ordinary steel, and many chemists consider it perfectly reliable in all cases. Others, however, prefer to use one of the methods given for the determination of phosphorus in iron, until the objection mentioned has been more thoroughly investigated. These methods are applied to steel in exactly the same way that they are to iron.

53. Drown's Method.—Weigh 2 grams of the drillings into a 12 or 16 ounce Erlenmeyer flask, add 75 cubic centimeters of nitric acid of 1.13 Sp. Gr., and, after violent action ceases, boil the solution for 2 or 3 minutes. Add 10 cubic centimeters of a potassium-permanganate solution containing about 12 grams to the liter, and continue the boiling until the pink color of the permanganate is destroyed. If the solution becomes clear, more permanganate must be added, and the boiling continued until a brown precipitate forms, when oxidation of phosphorus and carbon will be complete. Remove the flask from the heat for a moment, and add pure ferrous sulphate, in very small portions, until the precipitate is nearly dissolved; then boil it again for a few moments until the solution becomes perfectly clear. Remove the flask from the heat, and, after a minute or two, cautiously add 10 cubic centimeters of ammonia of .90 Sp. Gr., allowing the ammonia to run down the side of the flask, to avoid loss by spattering.

Boil the solution again for a few moments, to completely dissolve the iron precipitate; then insert a thermometer and allow the solution to cool to 85°. When at exactly this temperature, add 50 cubic centimeters of ammonium-molybdate solution, causing it to rinse off the thermometer as it flows into the flask. Give the flask a rotary motion for a few moments, then close it with a clean rubber stopper, and shake vigorously for 5 minutes. Allow the precipitate to settle for 15 minutes, filter, and wash thoroughly with the acid ammonium-sulphate solution described in Art. **42.** Wash as much of the precipitate as is convenient into the flask in which the precipitation was made, and dissolve the portion adhering to the paper with dilute ammonia, adding enough ammonia to dissolve all the precipitate; then wash the filter thoroughly with water, allow the ammonia and washings to run into the flask with the main part of the precipitate, and stir this until the precipitate is completely dissolved.

To this solution add about 12 grams of granulated zinc and 80 cubic centimeters of dilute sulphuric acid (1 part of

concentrate acid to 3 parts of water), place a small funnel in the neck of the flask, and stand it in a warm place for half an hour. Reduction will now be complete. Pour the solution through a large fluted filter, to separate the undissolved zinc. Rinse the flask with pure cold water, pour this on the filter, and, when it has run through, wash the filter by filling it once or twice with pure cold water. The filtrate, which should amount to from 300 to 400 cubic centimeters, is titrated at once with permanganate. As the permanganate is added, the solution gradually changes color and finally becomes colorless, when a few more drops of permanganate will impart a pink tinge to it, showing that the reaction is complete.

The solutions used in this determination are the same as those employed for the determination of phosphorus in iron, and the calculations are the same, except, in this case, 2 grams of the sample are taken.

This method is frequently modified by passing the solution of the yellow precipitate through a reductor instead of reducing it by heating in a flask with zinc and sulphuric acid.

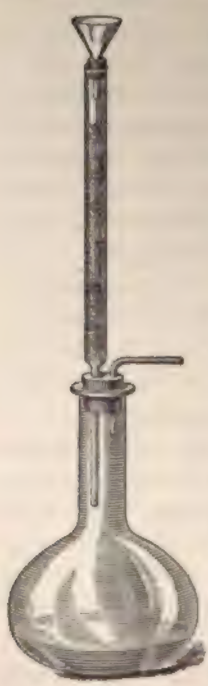


FIG. 9.

54. The Reductor.—At the present time, chemists are beginning to use a reductor quite largely to reduce solutions. A simple form of reductor is shown in Fig. 9. It is made as follows: Draw out a piece of glass tubing having an inside diameter of about $\frac{1}{2}$ inch; cut it off at a point about 15 inches from the end, and pass the small portion of the tube thus drawn out through one of the perforations of a rubber stopper fitted in a filtering flask. Drop in a few pieces of broken glass that are too large to pass through the small part of the tube, and, on this,

pour about 1 inch of coarse quartz sand that has been thoroughly cleansed (first, by boiling in hydrochloric acid, and then washing with distilled water) and thoroughly dried. On this, pour about 12 inches of pure granulated zinc that will pass through a 20-mesh but not through a 30-mesh sieve, and close the tube with a singly perforated stopper through which the stem of a funnel is passed. When a solution containing acid is poured in the funnel and drawn through the column of zinc, it is completely reduced at once, and, after washing the zinc thoroughly, is ready for titration.

To use the reductor in the determination of phosphorus by the method just given, dissolve the yellow precipitate in ammonia as directed, add about 50 cubic centimeters of dilute sulphuric acid (1 part acid to 3 parts water), dilute to 200 cubic centimeters, pour it in the funnel and draw it through the reductor by means of the filter pump. Wash all the solution out of the reductor by drawing 200 cubic centimeters of water through it, and titrate the solution at once with permanganate. The reagents used destroy some permanganate, and the amount thus used up must be determined by means of blanks, and deducted from the amount of permanganate used in the titrations. Several blanks, containing, approximately, the same amount of each of the reagents, and about the same amount of free acid, and having, approximately, the same bulk as the solution to be titrated, should be passed through the reductor and titrated. The first blank will generally use more permanganate than the succeeding ones; if this is the case, this result should be discarded, and the average of the others taken as the amount of permanganate to be deducted in each case.

CARBON.

55. Unlike any of the other elements contained in steel, carbon is known to exist in at least two conditions in the metal, in forms known as *graphite* and *combined carbon*. It is also believed that the combined carbon exists in two modifications, which are known as *hardening* and *cement*

carbon, and recent investigations have made this view appear almost certain.

It was noticed that when steel was worked, the results obtained in determining the combined carbon by the color method differed during the working, and that the properties of the steel also differed. It appears that the carbon shown by the color method is the part of this element present that imparts to the steel the property of becoming hard when tempered, and has received the name of hardening carbon. The color method is used almost exclusively for the determination of carbon in the routine work of steel-works laboratories, and, as the amount of graphite in steel is very small, and cement carbon, if such a form exists, is not known to have any influence on the properties of the metal, the results obtained by this method are usually reported merely as *carbon*.

From what has been said, it is evident that analytical chemistry supplies the means of distinguishing between at least two forms of this element in steel; viz., combined carbon and graphite, and it now seems probable that the color method only gives a part of the combined carbon, known as *hardening carbon*. For a long time the results obtained by the color method were supposed to represent all the combined carbon, and at present the percentage thus obtained is usually spoken of as the *combined carbon*. Accurate combustion methods are used for the determination of the total carbon, and the graphite; and from these results, the combined carbon is obtained by difference.

Two combustion methods are given. The first one—burning the carbonaceous residue in oxygen—is the most generally used, but the apparatus is costly, and the results obtained by the second method, the apparatus for which is inexpensive, are almost, if not quite, as accurate.

The carbon is not very often determined in pig iron, but if desired, either of the combustion methods here given may be used equally well for this purpose. In determining the carbon in pig iron, spiegeleisen, etc., 1 gram of sample and a corresponding amount of solvent should be used

Otherwise, the determinations should be carried out exactly as here given.

56. Total Carbon.—Weigh out 3 grams of the fine drillings, add 200 cubic centimeters of an acid solution of the double chloride of copper and potassium, and stir until the copper thrown out at first is all redissolved. The solution may be accomplished in a beaker, a 16-ounce Erlenmeyer flask, or a heavy glass jar. The drillings should be very fine for this determination, for fine drillings yield more uniform results, and, with coarse drillings, the process of solution becomes very tedious. If necessary, a few more drops of acid may be added, and the mixture heated to 80°. When the copper is all taken up by the solution, allow it to stand a few minutes to settle, and then proceed by one of the following methods:

1. *Combustion in Oxygen.*—Filter on a felt of pure ignited asbestos in a platinum boat shown in Fig. 10, leaving as much of the carbon as possible in the vessel. Add 10 cubic

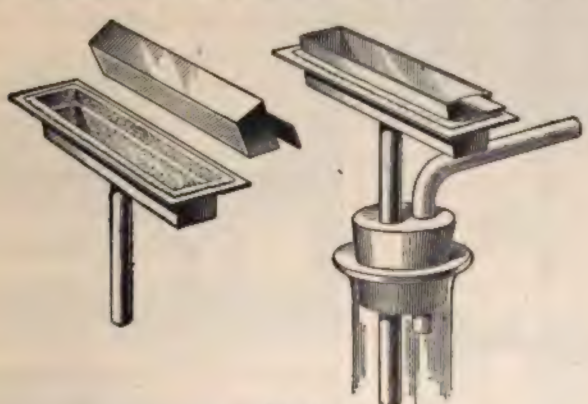


FIG. 10.

centimeters of hydrochloric acid of 1.1 Sp. Gr. to the vessel in which the sample was dissolved, and so manipulate that this acid shall touch every part of the vessel that has come in contact with the solvent liquid. Pour this acid on the felt in the boat, wash the carbon upon the felt by means of

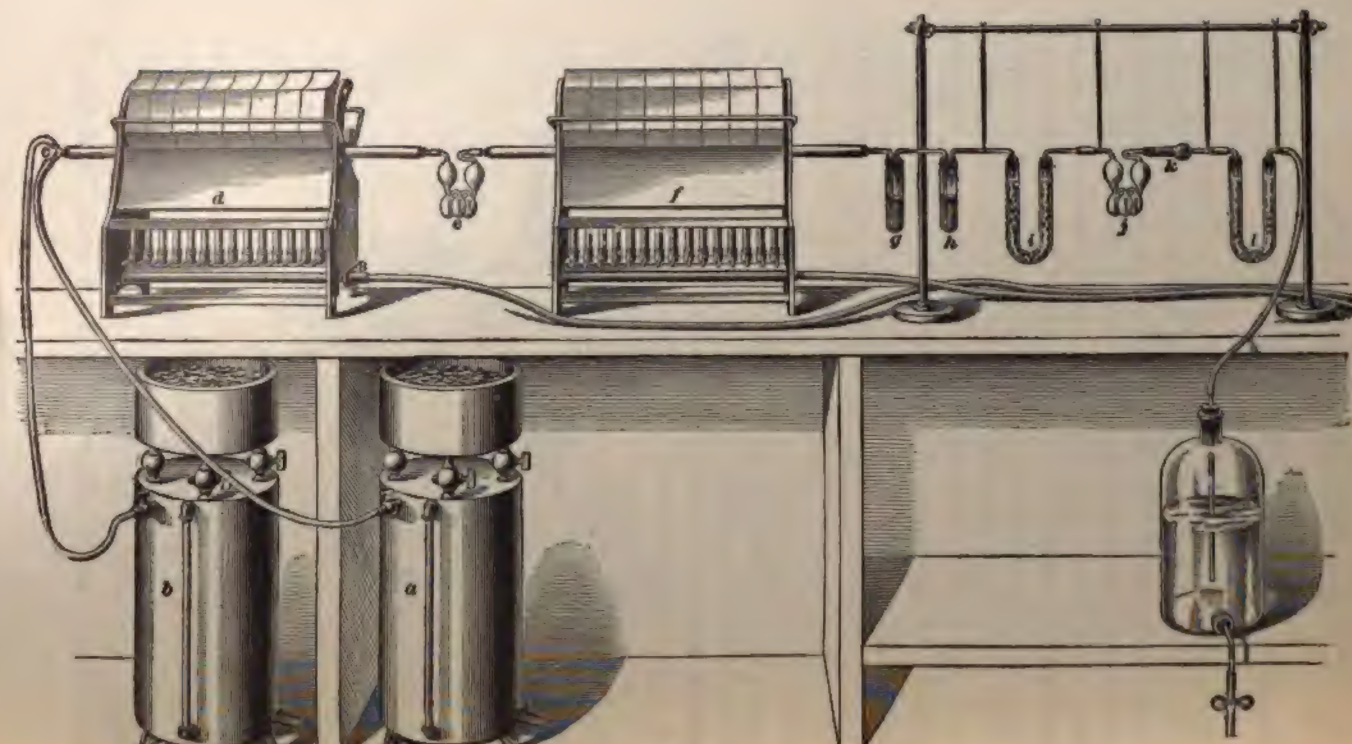


FIG. 11.

a wash bottle containing the same strength acid, and continue to wash with this acid until the washings come through perfectly clear. Then wash with water until the washings no longer react for hydrochloric acid when tested with silver nitrate. Dry the carbon, and filter by placing the boat in an air bath heated to about, but not above, 100°. While this is drying, weigh the absorption bulb and prolong, and place them in their proper position in the carbon train, which is shown in Fig. 11, and is prepared as follows:

The gasometers *a* and *b* contain air and oxygen, respectively, and are connected with the **V** tube *c*, which passes through a rubber stopper in the end of the porcelain tube fitted in the combustion furnace *d*, known as the preheating furnace. This tube should project at least 5 inches at each end of the furnace to prevent the rubber stoppers from becoming hot, and contains 8 or 10 inches of granulated copper oxide. Next comes the Geissler bulb *e* containing a strong solution of potassium hydrate, and known as the *purifying bulb.*

This is connected with the combustion tube proper, placed in the combustion furnace *f*. It is a tube of royal Berlin porcelain of $\frac{5}{8}$ inch internal diameter, and glazed inside and out. If a 14-inch Bunsen furnace is used, the tube should be from 24 to 28 inches long, and should be so placed that at least 5 inches of it project at each end of the furnace. To prepare this tube, place three or four tightly fitting disks of copper gauze towards one end of it, pour about 4 inches of granulated copper oxide on to them, and hold this in place by placing three or four more disks of copper gauze against it. Next to these, place a roll of pure silver gauze (about 2 inches in length) that nearly fills the tube, and place the tube in the furnace so that the gases evolved when the carbon is burned will pass through the roll of silver and the copper oxide. To the combustion tube attach a bubble tube *g* filled to about one-half its capacity with an acid solution of ferrous sulphate, to catch any free chlorine that may escape from the combustion tube, and connect this with a second bubble tube *h* filled to nearly one-half its capacity

with silver sulphate and water, to absorb any hydrochloric acid that may be mixed with the carbon dioxide. Tightly stoppered test tubes may be made to serve for the bubble tubes.

Next attach a U tube *i* filled with dry granulated calcium chloride, to dry the gas. To this, attach the weighed Geissler absorption bulb *j* containing a solution of potassium hydrate, and connect this with the weighed prolong *k*, which is filled with pure granulated calcium chloride that has been dried for half an hour in a platinum or porcelain dish over a Bunsen burner. Care must be taken not to fuse the calcium chloride while drying it. Different parts of the same lot of calcium chloride should be used to fill the prolong and the tube *i*, so that their drying power will be the same, and, whenever one of these tubes is refilled, the other should also be refilled from the same lot of calcium chloride. To the prolong, attach a U tube *l*, also filled with calcium chloride, to prevent any moisture from entering the combustion train from this end, and attach this U tube to an aspirator. All connections must be perfectly tight, so that gas can neither enter, nor escape from, the apparatus, and the ends of the glass tubes should come as near as possible to meeting inside of the rubber tubing used for connections. The pressure in the gasometers *a* and *b* should be so regulated that it will force air or oxygen through the purifying bulb *c*, but will not force them through the bubble tubes *g* and *h*.

When ready to commence a combustion, light the burners of the preheating furnace *d*, and gradually increase the temperature until the combustion tube containing copper oxide is red hot for 5 or 6 inches of its length. Then place the platinum boat containing the carbon next to the roll of silver foil in the combustion tube of the furnace *f*, and close the connection. Start the combustion by lighting enough burners, under the part of the tube in the furnace *f* that contains the copper oxide, to embrace about 3 inches of it in flame. Then see that the connection between the air gasometer and the preheating furnace is closed; turn on the oxygen, and regulate the aspirator so that about three bubbles per second

pass through the bulb *j*. The heat and aspiration must be so regulated that a steady current of oxygen passes through the bulb *c*, and there must not be back pressure at this point at any time during the operation. When the tube over the burners has become fairly red, turn on two more burners, and, when the tube has become red above these, turn on the burners one at a time, allowing the tube to become red above each burner before the next one is turned on, until the tube under the boat, and for 2 or 3 inches back of it, is embraced in flame.

After the tube has become red over all the burners lighted, allow the combustion to proceed for from 20 to 40 minutes, depending on the amount of carbon to be burned. Now, turn off every second burner, stop the supply of oxygen, turn on the air, and aspirate until about 1.5 liters of air have passed through the absorption bulb *j* at the rate of about three bubbles per second. While the aspiration is going on, turn out additional burners as fast as possible, without danger of breaking the tube from too sudden cooling. When the required amount of air has passed through, remove the absorption bulb and prolong, cover each end with a short piece of rubber tubing, one end of which is closed, with a piece of glass rod, stand them in the balance case 15 minutes to assume the temperature of the balance, and weigh. The increase in weight is the weight of carbon dioxide CO_2 produced by the combustion of the carbon, and contains 27.27 per cent. of carbon. When 3 grams of sample are taken, the weight of carbon dioxide, divided by 11, and the result multiplied by 100, gives the percentage of carbon in the sample.

Before making a determination by this method, two blanks should be run, and if the weight of the bulb and prolong changes to any great extent, something is wrong with the apparatus or chemicals. When two blanks are run without changing the weight of the absorption bulb and prolong more than 1 milligram, the last weight obtained in running the blank may be taken as the first weight in making a determination.

Dr. C. B. Dudley, to whom we are indebted for this

method, advises the use of a small absorption bulb and prolong, the whole, when filled and ready for use, to weigh from 50 to 60 grams.

2. *Combustion by Chromic Acid.*—Pour the solution in which the carbon is suspended through a felt of pure ignited asbestos in a filtering tube, prepared as shown in Fig. 5, leaving as much as possible of the carbon in the vessel in which solution was accomplished. To the carbon in this vessel, add 10 cubic centimeters of hydrochloric acid of 1.1 Sp. Gr. and so manipulate that the acid shall touch every part of the vessel that has come in contact with the solvent liquid. Pour this through the filter, wash the carbon on to the asbestos by means of a wash bottle containing acid of the same strength, and continue to wash with this acid until the washings are colorless as they come through. Then wash with distilled water for some time after the washings cease to give a reaction for hydrochloric acid when tested with silver nitrate. Transfer the carbon and asbestos to the flask *a*, using not more than 20 cubic centimeters of water to rinse in the carbon, and place the flask in position in the carbon train, shown in Fig. 12.

The flask *a* containing the carbon is fitted with a doubly perforated stopper, through one perforation of which the funnel tube *b* is passed. This is connected with the U tube *c*, which is filled with lumps of fused potassium hydrate, and acts as a purifying tube. Through the other perforation in the stopper of the flask *a*, is passed a tube connecting with the bubble tube *d*, containing pyrogallic-acid solution to absorb free chlorine and chlorine compounds of chromium. The bubble tube *e* is filled to a little less than half its capacity with an acid solution of ferrous sulphate, and *f* is a similar bubble tube, filled to a little less than half its capacity with an acid mixture of silver sulphate and water. The U tube *g* is filled with pure, dry, granulated calcium chloride.

Next comes the Geissler absorption bulb *h*, containing a strong solution of potassium hydrate, and to this is attached the prolong *i*, containing pure, dry, granulated calcium chloride. The absorption bulb and prolong are weighed

before they are introduced into the train. The prolong is connected with the **U** tube *j*, containing granulated calcium chloride, to prevent the entrance of moisture at the end of the train, and this is connected with an aspirator. A weighing **U** tube, filled to two-thirds its capacity with soda

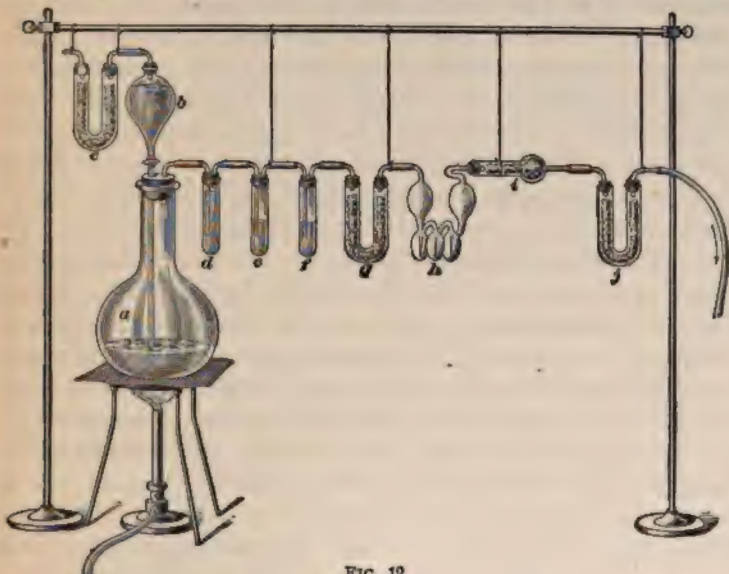


FIG. 12.

lime and the other one-third with granulated calcium chloride, is sometimes substituted for the absorption bulb and prolong, but this change is not to be recommended. In making connections, bring the ends of the glass tubes as near together as possible, under the rubber tubing, and be sure all connections are perfectly tight before commencing a determination.

When all is in readiness, remove the stopper from the separatory funnel *b*, introduce 10 cubic centimeters of a saturated solution of chromic anhydride CrO_3, allow it to flow into the flask *a* containing the carbon, and close the stop-cock. Now pour 100 cubic centimeters of concentrate sulphuric acid that has been heated nearly to boiling with a little chromic anhydride, into the separatory funnel, insert

the stopper carrying the purifying tube *c*, and, by turning the stop-cock, allow the acid to pass slowly into the flask *a*. Use the aspirator if necessary. Do not, under any circumstances, allow any gas to pass out through the separatory funnel. Keep air passing through the apparatus so that about three or four bubbles per second show in the absorption bulb. After a few moments, bring a burner, turned very low, under the flask *a*, and gradually increase the temperature until the acid mixture just begins to boil, and maintain this temperature for 10 or 15 minutes.

The carbon will now all be converted into carbon dioxide CO_2 by the oxidizing mixture. Gradually lower the flame of the burner, and, finally, turn it out, keeping the current of air through the apparatus constant, however. When about 1 liter of air has passed through the absorption bulb after the light is extinguished, disconnect the absorption bulb and prolong; cover each end with a short piece of rubber tubing, the other end of which is closed with a piece of glass rod, stand them in the balance case 15 minutes to assume the temperature of the balance, and weigh. The increase in weight is the weight of carbon dioxide CO_2 from the combustion of the carbon, and contains 27.27 per cent. of carbon. When 3 grams of sample are taken, the percentage of carbon may be calculated by dividing the weight of carbon dioxide by 11, and multiplying the result by 100.

This method is not generally considered as reliable as the first one, but the apparatus is simpler and less expensive, and when carefully performed by a skilled analyst, it yields very accurate results.

57. Graphite.—There are two methods for the determination of graphite in steel and pig iron that are more or less used, and both are here given. The first method, according to which the sample is dissolved in hydrochloric acid, is the most largely used, but the second method, in which the sample is dissolved by nitric acid, yields the most uniform, and probably the most accurate, results. The details of the two methods are as follows:

1. *Solution in Hydrochloric Acid.*—Dissolve 1 gram of pig iron, or from 5 to 10 grams of steel, in hydrochloric acid of 1.1 Sp. Gr., using 25 cubic centimeters for the pig iron, or 15 cubic centimeters for each gram of steel taken. Cover the beaker, and boil for 10 or 15 minutes. Filter on an asbestos felt in a platinum boat or filtering tube, washing the carbon on to the asbestos with a jet of hot water. Wash alternately on the felt with hot water and hydrochloric acid of 1.1 Sp. Gr., and then wash two or three times with hot water to remove the hydrochloric acid. Now wash the precipitate with a solution of potassium hydrate of 1.1 Sp. Gr. until all effervescence, due to silicon, ceases; wash the potassium hydrate out of felt with hot water, then wash twice with alcohol and twice with ether, and, finally, wash with hot water until the last trace of ether is removed from the precipitate and filter. If the carbon were filtered in a platinum boat, dry it at a temperature slightly below 100°, introduce it in a combustion tube, and burn it in oxygen, following the directions given in Art. **56,** 1. If a filtering tube were used, transfer the asbestos and carbon to a flask, using not more than 20 cubic centimeters of water to wash it in, and oxidize the carbon by means of chromic anhydride and sulphuric acid, following the directions given in Art. **56,** 2. In either case, the increase in weight of the absorption bulb and prolong is the weight of carbon dioxide obtained. From this, calculate the percentage of carbon, and call the result *graphite*.

2. *Solution in Nitric Acid.*—Weigh 1 gram of pig iron, or from 5 to 10 grams of steel, into a beaker, and dissolve in nitric acid of 1.2 Sp. Gr., using 25 cubic centimeters for the pig iron, or 15 cubic centimeters for each gram of steel taken. Stand aside until the residue settles, filter on a felt of ignited asbestos in a platinum boat or a filtering tube, washing the carbon on to the asbestos with hot water, and wash thoroughly on the filter with hot water. Then wash the residue with a solution of potassium hydrate of 1.1 Sp. Gr., follow this treatment by washing several times, alternately, with hot water and hydrochloric acid of 1.1 Sp. Gr., finally

washing the acid out of the filter with hot water. Next wash twice with alcohol, then twice with ether, and, finally, wash thoroughly with hot water. If a platinum boat were used in filtering, dry it at a temperature slightly below 100°, place it in a combustion tube, and burn in oxygen as directed in Art. **56,** 1. If the filtering funnel were used, transfer the asbestos to a flask, using less than 20 cubic centimeters of water to rinse the carbon in, and oxidize by means of chromic anhydride and sulphuric acid, following the directions given in Art. **56,** 2. In either case, calculate the percentage of carbon found from the weight of carbon dioxide, shown by the increase in weight of the absorption bulb and prolong, and call the result *graphite.*

58. Combined Carbon.—Having determined the total carbon and the graphite in a sample, the combined carbon is obtained indirectly by subtracting the graphite from the total carbon. This process would be much too long for general use in a steel-works laboratory, and, for the routine work, the color method is universally employed. This method, as we have already pointed out, probably only gives a part of the combined carbon, but, as this is not certain, and as the part shown by this method is supposed to be the only part exerting any important influence on the character of the steel, the results obtained by it are at present reported as combined carbon.

59. The Color Method for Carbon.—The color method depends on the fact that when a sample of steel is dissolved in pure nitric acid of 1.2 Sp. Gr., it imparts to the solution a depth of color that is directly proportionate to the amount of combined carbon it contains. Hence, the amount of combined carbon may be determined by comparing the color of the solution of the sample to be analyzed with the color of the solution of a sample in which the carbon has been carefully determined by combustion methods. There are several things, however, that have an influence on the color produced. The method of solution, the chemical composition

of the steel, the physical treatment it has received, and the process by which it was manufactured, all appear to have their influence on the color produced; hence, the standard steel should have, approximately, the same composition, should have been manufactured by the same process, and received the same physical treatment, and should be dissolved in the same manner and at the same time as the samples to be tested. The best results are obtained when both the standard steel and the samples for analysis are taken as the metal is poured into the mold.

A number of modifications of this method have been published, and are used, and many of them have advantages for steels of certain composition. One that the writer has used very largely and found to give excellent results with samples of any composition, is as follows:

Weigh out .5 gram of the standard steel, and exactly the same weight of each of the samples for analysis; transfer each to a properly labeled test tube 7 inches long by $\frac{7}{8}$ inch in diameter, and stand the test tubes in a rack similar to the one shown in Fig. 13, in which *a* is a copper disk perforated to receive the test tubes, and *b*, which is joined to the copper disk by the supports, is a disk of coarse copper gauze for the test tubes to rest on.

FIG. 13.

Place the rack containing the test tubes with the samples in a vessel of cold water, and add 10 cubic centimeters of nitric acid of 1.2 Sp. Gr. to each. The nitric acid used for this purpose should be perfectly pure, and under no conditions must it contain chlorine or hydrochloric acid. When violent action ceases, place the rack containing the tubes in a water bath containing boiling water, and leave them in this for 5 minutes after all the steel is dissolved, shaking the tubes occasionally, if necessary, to prevent the formation of a film of iron oxide. Stand the rack in a dish of cold water 2 minutes for the solutions to cool, decant the standard into a graduated reading tube of colorless glass, and dilute it until

1 cubic centimeter of the solution represents .01 per cent. of carbon.

Thus, if the standard contains .15 per cent. of carbon, dilute the solution to 15 cubic centimeters with distilled water. Now decant one of the samples to be tested into a similar reading tube that has exactly the same dimensions as the one containing the standard, and dilute it until its color exactly matches the standard. Each cubic centimeter of this will now represent .01 per cent. of carbon. Thus, if the solution amounts to 18 cubic centimeters, the sample contains .18 per cent. of combined carbon. As soon as the reading is taken, this tube should be emptied, rinsed, a second sample introduced, diluted, and read in the same way.

Not more than 10 samples should be analyzed at once, and the readings should be taken as rapidly as possible, for the standard gradually loses its color when allowed to stand. The colors should be compared in diffused light. It is best to stand in front of a window facing north, when comparing them, and a piece of wet filter paper pressed against the back of the tubes sometimes helps to determine the exact tint. A camera, shown in Fig. 14, is sometimes used for this purpose. It consists of a box of light wood, blackened inside. About 1 inch from the end *b*, a piece of ground glass is inserted. Just back of this, two openings are made in the top to receive the comparison tubes. By viewing the solutions from the end *a*, the tints are determined.

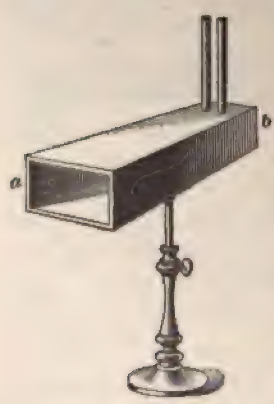


FIG. 14.

If the steel contains more than .4 per cent. of combined carbon, it is best to use samples weighing .2 or .3 gram, and dissolve them in 5 or 6 cubic centimeters of nitric acid. As it takes some time, as a rule, to dissolve samples containing so much carbon, it is best to place small glass bulbs in the mouth of the tubes to prevent loss of acid by evaporation

during solution. In reading such samples, dilute the standard until 1 cubic centimeter represents .02 or .03 per cent. of carbon, dilute the sample until the colors agree, and multiply the reading by the factor. For instance, let us suppose that the standard steel contains .6 per cent. of carbon, and the solution is diluted to 20 cubic centimeters. Each cubic centimeter will then represent .03 per cent. of carbon. If the solution of a sample, when diluted to match this, amounts to 22 cubic centimeters, it contains $22 \times .03 = .66$ per cent. of combined carbon.

SOLUTIONS FOR CARBON DETERMINATIONS.

60. Copper Potassium Chloride.—To make the acid copper potassium-chloride solution, used in dissolving the sample for the determination of total carbon, dissolve 1 pound of the solid salt in 1,300 cubic centimeters of water, and, if the solution is not perfectly clear, filter through ignited asbestos. To the clear solution or filtrate, add 100 cubic centimeters of pure concentrate hydrochloric acid, and stir well to secure thorough mixing.

61. Potassium Hydrate.—The potassium-hydrate solution used in the absorption bulb, and in the purifying bulb, is made by dissolving pure solid potassium hydrate in a small amount of water, and diluting the solution until it has a specific gravity of 1.27 when cold. About 1 liter of this solution may be made from 400 grams of solid potassium hydrate.

62. Ferrous Sulphate.—To make the acid solution of ferrous sulphate, dissolve the pure crystallized salt in water, making almost a saturated solution, and, to every 50 cubic centimeters of this solution add 5 drops of concentrate sulphuric acid. This solution is used to absorb free chlorine. It appears to form hydrochloric acid, and to retain most of the acid thus formed.

63. Silver Sulphate.—Dr. Dudley recommends the following method for the preparation of this solution:

Precipitate silver carbonate by adding sodium carbonate to a solution of silver nitrate. Filter and wash thoroughly. By means of a little water, transfer the precipitate to the bottle in which it is to be kept, and add sulphuric acid—at last, drop by drop—while agitating the mixture, until the carbonate is completely decomposed and the liquid is distinctly acid to test paper. To fill the bubble tube, shake the bottle well and pour enough of the milky mixture into the tube so that about ¼ inch of solid will settle to the bottom; then add water to fill the tube to nearly one-half its capacity. This solution absorbs any hydrochloric acid that may pass over from the ferrous-sulphate tube.

64. Pyrogallic-Acid Solution.—This solution is made up by mixing .2 gram of pyrogallic acid, 5 grams of neutral potassium oxalate, and 3 grams of pure sodium chloride, and dissolving the mixture in water sufficient to make 20 cubic centimeters of solution. When dissolved, add 2 drops of concentrate sulphuric acid, which must render the solution distinctly acid to test paper. This solution absorbs free chlorine and chlorochromic acid. It may liberate hydrochloric acid, as it tends to form this acid from the oxides of chlorine.

ANALYSIS OF COAL AND COKE.

PROXIMATE ANALYSIS.

65. A proximate analysis of coal is nearly always required, and, although the results obtained are, to a great extent, merely comparative, yet, when the directions given are strictly followed, the results obtained are accurate enough to be of great service in determining the value of the coal for various purposes. It is of the utmost importance that the directions given should be followed exactly in every case, for slight variations in the method give large differences in the results, and as the results, so far as *moisture*, *volatile combustible matter*, and *fixed carbon* are concerned, are only

comparative, they must be obtained under exactly the same conditions in every case if they are to be of any value.

In selecting a sample, about 5 pounds of the coal should be taken, exercising care, of course, to get a sample representing the whole quantity. Break this up and quarter it down until a sample weighing about 100 grams is left. Pulverize this, and keep it in a tightly stoppered bottle until analyzed. The quartering and pulverizing should be carried out as rapidly as possible, to prevent the absorption or loss of water, and, as coal in the powdered form changes in other respects, especially when exposed to air, it should be kept in a tightly stoppered bottle, and the analysis should be made as soon as convenient after the sample is taken. A method of analysis that gives concordant results, and is probably more largely used than any other at the present time, is as follows:

66. Moisture.—When coal is dried at a temperature slightly above 100°, it loses in weight for a time, and then begins to grow heavier. Consequently, we cannot dry the sample in the ordinary way until a constant weight is obtained, and it is necessary to dry all samples for a certain time at a fixed temperature to obtain concordant results. The following method of doing this has been generally adopted: Weigh 1 gram of the pulverized sample into a platinum crucible weighing from 20 to 30 grams and having a tight-fitting cover. Place the crucible, uncovered, in an air bath having a temperature ranging from 105° to 110°, and heat it at this temperature for exactly 1 hour. Place the crucible in a desiccator, cover it, and allow it to cool. As soon as cool, weigh covered, and call the loss in weight *moisture*.

67. Volatile Combustible Matter.—Weigh 1 gram of the pulverized sample into a clean platinum crucible of the same size as that used in the determination of moisture. Place the cover on tight, and heat over a good Bunsen burner for exactly 3.5 minutes; then bring a blast lamp under the crucible and heat it for exactly 3.5 minutes more.

Do not allow the crucible and contents to cool while changing burners, but keep the Bunsen burner under the crucible until the flame from the blast lamp is playing on it. Cool the crucible in a desiccator and weigh as soon as cool. From the loss in weight caused by this treatment, subtract the amount of moisture found, and call the remainder *volatile combustible matter*. This determination should always be made on a fresh sample of coal, and not on the sample used for the determination of moisture.

68. Fixed Carbon and Ash.—After weighing the crucible for the determination of volatile combustible matter, draw the cover a little to one side, place the crucible in an inclined position on a triangle, as shown in Fig. 5, *Quantitative Analysis*, Part 2, place a good Bunsen burner under it, and heat until the carbon is completely burned off. This operation is likely to prove tedious, and may be hastened by letting the crucible cool from time to time, and by stirring the contents with a stout piece of platinum wire, taking care, of course, not to lose any of the material in the crucible while stirring it up. Care must also be taken not to produce too strong a current of air in the crucible while heating it, as, in this way, particles may be carried out, and a fictitious value given to the coal or coke by the apparent increase in fixed carbon and decrease in ash. When the residue in the crucible no longer shows any unburned carbon, heat it a few minutes longer, then cool it in a desiccator and weigh. The difference between this weight and the last one is the weight of fixed carbon in the sample, and the substance remaining in the crucible is ash. The percentages of the different constituents are, of course, calculated in the usual manner, and, as 1-gram samples are taken, the calculations are very simple. The sum of the percentages of fixed carbon and ash is approximately the percentage of coke that may be obtained from the coal.

69. Sulphur.—There are two methods in quite general use for the determination of sulphur in coal and coke. They

are known as the fusion method and Eschka's method. The fusion method is the older, and, until quite recently, was used almost exclusively, but at the present time Eschka's method is probably the more generally used. Both methods are given herewith.

1. *The Fusion Method.*—Weigh out 1 gram of the pulverized sample, mix it thoroughly with 9 grams of sodium carbonate and 5 grams of potassium nitrate, by grinding them together in a mortar, and transfer the mixture to a large platinum crucible. Rinse out the mortar by grinding in it about 1 gram of sodium carbonate, and pour this on the mixture in the crucible. Cover the crucible and heat it over a Bunsen burner. A very gentle heat should be applied at first, and the temperature should be raised gradually, removing the cover from time to time to see that the fusion does not boil over. None of the fusion must be allowed to get on the outside of the crucible, or it will absorb sulphur from the burning gas and cause the analysis to yield erroneous results. For the same reason, care should be taken not to allow the gaseous products of the combustion to enter the crucible. When the contents of the crucible are in a state of quiet fusion, run the mass well up on the sides of the crucible, and allow it to cool.

Dissolve the fusion out of the crucible with hot water, wash the crucible thoroughly, boil the fusion until it is completely disintegrated, filter off the insoluble matter, and wash it thoroughly on the filter with hot water. Acidulate the filtrate with hydrochloric acid, and evaporate to dryness. Moisten the residue with a few drops of hydrochloric acid, add about 100 cubic centimeters of water, and heat to boiling. Filter, wash the filter well with hot water, dilute the filtrate to about 400 cubic centimeters, heat it to boiling, and precipitate the sulphur by adding from 10 to 20 cubic centimeters of a 10-per-cent. solution of barium chloride. Stand the solution in a warm place for the precipitated barium sulphate to settle, filter through a paper, or an asbestos felt in a Gooch crucible, ignite moderately, observing the precautions necessary in the ignition of this precipitate, cool, and weigh

as barium sulphate $BaSO_4$, which contains 13.73 per cent. of sulphur.

A blank determination should be made with each new lot of chemicals, using the same amount of each that is used in the actual determination; and the weight of barium sulphate that is obtained from the blank determination is subtracted from the weight obtained in each sulphur determination of the coal, before the percentage of sulphur in the coal or coke is calculated.

2. *Eschka's Method.*—Weigh out 1 gram of the pulverized coal or coke and mix it intimately with 1.5 grams of Eschka mixture (see Art. **71**) by grinding them together in a mortar. Transfer this mixture to a platinum crucible having a capacity of about 30 cubic centimeters, rinse out the mortar by grinding in it about .5 gram of Eschka mixture, and pour this on to the mixture in the crucible. Place the crucible in a slanting position, with the cover drawn aside, as shown in Fig. 5, *Quantitative Analysis*, Part 2, and apply very gentle heat at first, allowing the flame to strike the crucible near the top of the mixture. If the gas ordinarily used contains sulphur—and all coal gas does contain this element—an alcohol lamp should be substituted for the Bunsen burner. After a time, raise the temperature and move the burner towards the bottom of the crucible, finally heating until the crucible shows a dull-red color for about one-third of the way up from the bottom. Now stir the mixture with a platinum wire at frequent intervals until the coal appears to be completely burned. This will usually require about 1 hour.

As coke burns much more slowly than coal, and contains no volatile constituents, a stronger heat may be applied at once when working with it. Allow the crucible to cool, add about 1 gram of ammonium nitrate to the contents, and mix it in thoroughly by means of the piece of stout platinum wire, or platinum rod, used in stirring the mixture. Cover the crucible, heat it cautiously until the ammonium nitrate is decomposed, and, finally, raise the temperature until the crucible is heated to bright redness. Allow it to cool, extract the contents by boiling with water, remove the crucible and

wash it with water, allowing the washings to run back into the dish. Break up with a stirring rod any lumps that may remain in the solution, and boil until the mass is completely disintegrated. Filter off the insoluble matter, wash it thoroughly with hot water, acidulate the filtrate with hydrochloric acid, and evaporate to dryness. Moisten the residue with a few drops of hydrochloric acid, add 100 cubic centimeters of water, and heat to boiling to dissolve the residue. Filter off any insoluble matter, and wash it thoroughly with hot water. Heat the filtrate, which should amount to about 250 cubic centimeters, to boiling, and precipitate the sulphur with from 10 to 20 cubic centimeters of barium-chloride solution.

Stand the beaker in a warm place for the precipitate to settle; filter, wash thoroughly with hot water acidulated with a few drops of hydrochloric acid, ignite moderately, and weigh as barium sulphate $BaSO_4$, which contains 13.73 per cent. of sulphur. The directions given in Art. **32** should be followed in filtering and igniting this precipitate.

Although chemicals that are absolutely free from sulphur may be obtained for this determination in the market, a careful blank should be run with each new lot of reagents, for some so called C. P. ("chemically pure") chemicals are not strictly as represented.

70. Phosphorus.—Weigh out 10 grams of the powdered sample in a platinum crucible, and burn off the carbon. This may be done as in the determination of fixed carbon, or, if the laboratory contains a muffle furnace, the crucible may be placed in this and the carbon allowed to burn, leaving the crucible uncovered in this case. As samples of anthracite coal and coke burn very slowly, the process is sometimes hastened by burning in oxygen. This may be done by covering the crucible with a perforated piece of platinum foil, and leading a slow current of oxygen through this perforation, in the same way that the hydrogen is led into the Rose crucible in the ignition of copper sulphide (see Art. **18**, *Quantitative Analysis*, Part 1).

When all the carbon is burned off, treat the residue with

concentrate hydrochloric acid, dilute the solution with water, filter, wash thoroughly with hot water, and stand the filtrate aside. Dry the filter and residue, burn off the paper, and fuse the residue with about six times its weight of pure sodium carbonate. Dissolve the fusion in water, filter off the insoluble matter, and wash it well with hot water. Acidulate the filtrate with hydrochloric acid, and evaporate to dryness. Moisten the residue with a few drops of hydrochloric acid, add about 100 cubic centimeters of water, boil a few minutes, and filter. Wash the insoluble matter on the filter with hot water, and add this filtrate to the first one. To the combined filtrates, add a little ferric chloride that must be free from phosphorus, and render the solution slightly alkaline with ammonia; then acidulate it with acetic acid, and boil a few minutes.

The precipitate formed will contain all the phosphorus. Filter and wash once with boiling water. Dissolve the precipitate in hydrochloric acid, and evaporate the solution to a small bulk, taking care not to allow an insoluble scale of iron oxide to form. Then add 5 cubic centimeters of concentrate nitric acid, and follow this in a few moments with 30 cubic centimeters of water. Filter into a flask and wash the filter well with a 2-per cent. solution of nitric acid. To the solution in the flask, add 30 cubic centimeters of concentrate ammonia, and then about 1 cubic centimeter of concentrate nitric acid in excess of the amount required to dissolve the precipitate formed. Heat the solution to exactly 85°, add from 50 to 75 cubic centimeters of ammonium-molybdate solution, agitate the solution for 5 minutes, allow it to stand 15 or 20 minutes for the precipitate to settle, filter, wash, and proceed with the determination by one of the methods given in Art. **38** *et seq.* It is best to use the gravimetric method, weighing as magnesium pyrophosphate, for this determination, and the directions given in Art. **16** should be followed. When using this method, if the percentage of phosphorus is low, it is best to allow the solution to stand about 1 hour for the yellow precipitate to settle.

REAGENTS FOR COAL ANALYSIS.

71. Eschka Mixture.—Weigh out a convenient quantity of pure magnesium oxide that must be free frem sulphur, and that has been previously ignited to expel all moisture; add to this half its weight of pure dry sodium carbonate, grind them together until they are thoroughly mixed, and keep the mixture in a tightly stoppered bottle. A bottle with a ground glass stopper is preferred for this purpose; at all events, the mixture must be kept dry.

ANALYSIS OF CLAY.

CHEMICAL ANALYSIS.

72. Clay is principally a product of the decomposition of feldspathic rocks, and is essentially a mixture of the silicates of aluminum, calcium, magnesium, sodium, and potassium with silica. The silicates are hydrated, so that clay ordinarily contains from 6 to 14 per cent. of combined water, and nearly all, if not all, samples contain small quantities of iron. A mechanical analysis of clay to separate the coarse from the fine parts, and a careful examination to determine the condition in which the silica exists, as well as a number of tests of physical properties, are sometimes required; but for these the student is referred to a more exhaustive treatise on the subject, and only the chemical analysis will be given here. This is ordinarily all that is required to determine the fitness of clay for the manufacture of bricks, or for use in metallurgical operations. Clay that is to be used for the manufacture of firebrick, or in metallurgical processes where it is exposed to great heat, should not contain much iron, potassium, or sodium, as these constituents fuse rather easily. The best clay for these purposes does not contain more than 1 per cent. of either of the alkalies, or more than 2 per cent. of iron oxide. The determinations usually made are, moisture, combined water.

silica, alumina, iron oxide, calcium oxide, magnesia, and the alkalies.

73. Determination of Moisture.—Grind from 5 to 10 grams of the clay to an exceedingly fine powder in an agate mortar, weigh it on a watch glass, transfer the watch glass with the sample to an air bath, and heat it for one hour at a temperature ranging from 100° to 105°. Remove it to a desiccator, and weigh as soon as cool. Return the watch glass with the sample to the air bath, heat it 15 minutes longer at the same temperature, cool in a desiccator, and weigh again as soon as cool. If this weight differs from the previous one, the sample must be heated again, and this must be continued until a constant weight is obtained. From the loss in weight when the sample is dried at this temperature, calculate the percentage of moisture in the sample.

As soon as the sample is weighed, transfer it to a clean dry bottle or tube, and keep it tightly stoppered, to be used for the other determinations. As the other constituents are determined in the dry sample, the moisture is not included in the regular report, but is reported as a separate item.

74. Determination of Combined Water.—Weigh 2 grams of the dried sample in a platinum crucible, and ignite it for 20 minutes with the cover on, keeping the crucible at a red heat. Cool in a desiccator and weigh as soon as cool. Ignite 5 minutes longer, cool in a desiccator, and again weigh as soon as cool. If this weight differs from the previous one, the ignition must be continued until a constant weight is obtained. From the loss in weight, calculate the percentage of combined water in the sample. This method yields accurate results with most samples, but if the clay contains much organic matter or pyrite, it cannot be used. In such cases, the water should be determined by the method described in Art. **132**, *Quantitative Analysis*, Part 2.

75. Determination of Silica.—Weigh out 1 gram of the dry sample, mix it thoroughly with 10 grams of fusion mixture, consisting of equal parts of the carbonates of sodium and potassium, and introduce the mixture into a large platinum crucible. Heat this over a good Bunsen burner until it begins to cake together, and then heat over a blast lamp until it has been in a state of quiet fusion for some time. The fusion may now be removed from the crucible by quickly pouring the molten mass into a clean dry platinum dish floating on cold water. The fusion, upon striking the cold platinum, solidifies quickly and will not adhere to the dish. The small quantity of fusion remaining in the crucible can be mostly removed by hot water, and the small quantity remaining after this treatment is readily dissolved out by hydrochloric acid.

At all events, dissolve the fusion in water, acidify the solution with hydrochloric acid, evaporate to dryness, and heat at about 130° until the odor of hydrochloric acid is no longer given off. To the residue, add 15 cubic centimeters of concentrate hydrochloric acid, and heat gently to dissolve the iron; then add 50 cubic centimeters of water, heat to boiling, allow the insoluble matter to settle, and filter. Wash thoroughly on the filter with hot water, wrap the paper around the precipitate, place them in a platinum crucible, and, after burning off the paper over a Bunsen burner, ignite intensely over a blast lamp, cool in a desiccator, and weigh as silica. From this weight, calculate the percentage of silica in the sample.

76. Determination of Alumina.—Heat the filtrate from the silica to boiling, add a few drops of concentrate nitric acid, then add a slight excess of ammonia while stirring continuously, and continue to boil for a few moments, taking care that the solution remains faintly alkaline. As soon as the precipitate has settled, decant as much as possible of the clear liquid through a filter, then transfer the precipitate to the filter, and wash it thoroughly with hot water. Wrap the filter around the precipitate, place them in a

platinum crucible, and, after burning off the paper over a Bunsen burner, ignite strongly over a blast lamp, cool in a desiccator, and weigh. The precipitate now consists of the oxides of aluminum and iron, $Al_2O_3 + Fe_2O_3$. After determining the ferric oxide in the sample, deduct this from the mixed oxides, and the remainder will be alumina.

The iron may be determined by fusing the precipitate of mixed oxides with acid potassium sulphate, dissolving the fusion, reducing the iron, and titrating with permanganate, as directed in Art. **141**, *Quantitative Analysis*, Part 2, or the iron may be determined in a separate portion of the sample, as directed in Art. **79.**

77. Determination of Calcium.—If the filtrate from the alumina greatly exceeds 250 cubic centimeters in volume, evaporate it to about this amount; then, to the gently boiling solution, add 5 cubic centimeters of concentrate ammonia, and a moderate excess of ammonium oxalate, continue the boiling for a few minutes, and then stand the solution in a warm place for 4 hours, to allow the precipitate to collect and settle. Slightly more ammonium oxalate than is required to convert all the calcium and magnesium into oxalates must be added, but a very large excess is to be avoided. Filter off the precipitated calcium oxalate, and wash it thoroughly with hot water to which a few drops of ammonia have been added. Wrap the precipitate in the filter, place them in a platinum crucible, and, after heating gently over the Bunsen burner, to drive off moisture and burn the paper, ignite at the full power of the blast lamp until a constant weight is obtained. It is a good plan to allow the precipitate to cool, after igniting it for 5 or 10 minutes over the blast lamp, and, when cool, to moisten it with a few drops of water; then, after heating it gently to drive off the water, ignite it again at the full power of the blast lamp for 10 minutes before weighing it the first time. When a constant weight is obtained, the precipitate is calcium oxide, and from this weight, the percentage of calcium oxide in the sample is obtained.

78. Determination of Magnesium.—Evaporate the filtrate from the calcium oxalate to about 200 or 250 cubic centimeters, cool the solution by standing the beaker in cold water, and, when cold, add an excess of sodium-ammonium phosphate, drop by drop, while stirring continuously. When all the reagent has been added, pour in a quantity of concentrate ammonia equal to about one-third the volume of the solution. Stir the solution several times after the ammonia is added, and then stand it in a cool place for 6 hours, for the precipitate to separate. Filter and wash the precipitate thoroughly with cold one-third-strength ammonia containing a little ammonium nitrate. Dry the precipitate in an air bath, remove it as completely as possible from the filter, and burn the latter in a weighed crucible. When this is cool, add the precipitate, ignite at the full power of the blast-lamp for 10 minutes, cool in a desiccator, and weigh as magnesium pyrophosphate $Mg_2P_2O_7$. From this, calculate the percentage of magnesium oxide MgO in the sample.

79. Determination of Iron.—The iron may be determined in the precipitate of alumina and iron after it has been weighed, by fusing it, and proceeding as directed in Art. **76**, or it may be determined in a fresh sample as follows: Fuse 1 gram of the sample with mixed carbonates, dissolve the fusion in water and hydrochloric acid, and evaporate to dryness, just as in the determination of silica. Moisten the residue with hydrochloric acid, dissolve it in water, filter off the silica, and wash it well with hot water, adding a few drops of hydrochloric acid with the fourth or fifth quantity of wash water. Heat the filtrate to boiling, add a few drops of concentrate nitric acid, and, after boiling the solution a few moments longer, precipitate the iron and alumina with ammonia.

As soon as the precipitate settles, filter and wash once or twice with hot water. Dissolve the precipitate in the least necessary quantity of hydrochloric acid, reduce the iron in this solution with zinc, and titrate with potassium permanganate in the usual way. A blank must be run to determine

the amount of permanganate used up by the reagents. The difference is the amount used by the iron. From the amount of iron found in this way, calculate the percentage of ferric oxide in the sample. The ferric oxide found by this determination is deducted from the alumina and iron oxide previously determined, to obtain the percentage of alumina.

80. Determination of Alkalies.—Weigh out 1 gram of the sample, place it in an agate mortar, add 1 gram of pure ammonium chloride, and grind them together intimately; then add 7 grams of pure calcium carbonate, and grind the contents of the mortar together with the pestle until thoroughly mixed. Now introduce 1 gram of pure calcium carbonate in the bottom of a large platinum crucible, pour the mixture from the mortar on this, and cover the mixture with 1 gram more of the pure calcium carbonate. Cover the crucible, place it over a Bunsen burner, turned very low at first, but gradually increase the temperature, and, finally, heat to dull redness for an hour. Treat the contents of the crucible with hot water in a porcelain dish, breaking up any hard lumps with an agate pestle, if necessary. After boiling until the mass is completely disintegrated, filter off the insoluble matter, and wash it with hot water until a small test of the washings, collected in a test tube and acidified with nitric acid, only shows a faint cloudiness when silver nitrate is added. Evaporate the filtrate to about 75 cubic centimeters, remove it from the flame, add a few drops of pure ammonia, and then a strong solution of pure ammonium carbonate as long as a precipitate forms. Stir well and allow the precipitate to settle. Filter, receiving the filtrate in a porcelain dish, and wash with hot water rendered faintly alkaline with ammonia until the washings come through free from chlorine.

Sometimes a very little ammonium carbonate is also added to the wash water. Add a few drops of hydrochloric acid to the filtrate, evaporate to a small bulk, and transfer to a small platinum dish, washing in the last portions with a little

distilled water. Evaporate to dryness on a water bath, and, after heating gently to expel all water, increase the temperature to drive off ammonium compounds, finally heating the dish to very faint redness. When cool, dissolve the residue in a little water, add a drop or two of ammonia, then a few drops of ammonium carbonate, and heat on the water bath for a few minutes. Filter, and wash with water rendered faintly alkaline with ammonia, receiving the filtrate in a small, weighed, platinum dish. Acidulate the filtrate with a few drops of hydrochloric acid, evaporate to dryness on the water bath, then place the dish in an air bath and raise the temperature from 100° to about 140°. Remove the dish from the air bath, and heat it cautiously over a burner, to expel ammonium salts, finally heating the dish until it shows a faint red tinge. Cool in a desiccator, and weigh as soon as cool. The weight of the combined chlorides of sodium and potassium is thus obtained.

Dissolve the residue in a few cubic centimeters of water, add a nearly neutral solution of platinum chloride in sufficient quantity to convert the chlorides of sodium and potassium into the corresponding double chlorides of platinum and these metals, and have a moderate excess remaining. Place the dish on a water bath in which the water is maintained at as near the boiling point as possible, and evaporate the contents to a pasty consistency. Add 35 cubic centimeters of 80-per-cent. alcohol, and stand the dish in a warm place for an hour, stirring the contents occasionally to dissolve the double chloride of sodium and platinum. Filter on a weighed paper, wash thoroughly, but not excessively, with 80-per-cent. alcohol, dry in an air bath at 130° until a constant weight is obtained, and weigh as potassium-platinum chloride K_2PtCl_6.

From the weight of potassium-platinum chloride obtained, calculate the weight of potassium chloride, and subtract this from the weight of the mixed chlorides. The remainder is the weight of sodium chloride. Calculate the sodium and potassium to the oxides, Na_2O and K_2O, and report them as such.

EXAMINATION OF WATER.

PRELIMINARY REMARKS.

81. The process of analysis to be pursued in the examination of water, depends on the purpose for which the water is to be used. It is most frequently analyzed to determine its fitness for drinking or culinary purposes, or as a boiler supply. As the fitness of a water for these two purposes depends on entirely different conditions, a water that would be well adapted to one purpose might be absolutely unfit for the other. The subject is therefore usually divided into the analysis of potable water, and the analysis of water for boiler supply, and this division of the subject will be observed in the present work. A chemist is occasionally called on to determine the fitness of a water for some particular manufacturing process, and, although we cannot treat every possible case, the student that masters what is given here will be able to answer all such questions for the determinations necessary, and the methods of making them will readily suggest themselves.

There are several methods of reporting the results of water analyses. The oldest method, and one that is still very largely employed, is to report the amount of each constituent in grains per gallon. This method is likely to cause confusion, as there are several gallons having different capacities. The English Imperial gallon contains 70,000 grains, and the United States gallon contains 58,318 grains. By far the most rational method of reporting results, is in parts per million, or, what is the same thing, in milligrams per liter, or to report them in parts per hundred thousand. If results are reported in parts per million, or milligrams per liter, they can readily be changed to grains per gallon, if desired, by means of a very simple calculation. One liter of water contains 1,000,000 milligrams, and one U. S. gallon contains 58,318 grains. Hence, the number of milligrams

in a liter of a constituent, multiplied by 58,318, and the result divided by 1,000,000, gives the number of grains of that constituent in a U. S. gallon of the water. If this method of reporting results is adopted, it should always be stated in the report that the U. S. gallon is used.

POTABLE WATER.

82. The principal determinations usually made to determine the fitness of a water for drinking and cooking purposes are: chlorine; free and albuminoid ammonia; oxygen consumed in the moist combustion process; and nitrates, nitrites, and poisonous metals. In addition to these, the total solids and the hardness are frequently determined.

It is difficult to say how much of any one of these constituents may be found in a water without condemning it, but each furnishes valuable indications, and, taken together, give a fairly good idea of the purity of the water. Obviously, impurities coming from some sources are much more injurious than if coming from others. Thus, the organic matter coming from sewage would be more injurious than the same quantity coming from vegetable matter, and, in giving an opinion as to the quality of a water, a chemist must use his judgment. If possible, the chemist should select the sample himself, in order that he may examine the surroundings, and see from what sources pollution may come. In many cases, this will aid him materially in forming an opinion in regard to the quality of the water, for, if the water is found to contain a small amount of impurity, he will know whether it is likely to be dangerous or not.

83. Collecting a Sample.—The amount of water to be collected as a sample will depend on circumstances, but, in no case, should less than about 2.5 liters be taken. It is best to collect and preserve the sample in a large glass-stoppered bottle. A 5-liter bottle with a ground-glass stopper is very handy for this purpose, but in the absence of such a

bottle, a large bottle or demijohn with a new, clean cork stopper may be used. Too great stress cannot be laid on the fact that in collecting samples and analyzing the water, strict cleanliness is absolutely essential. The reason will be obvious when the student considers that in most cases only fractions of 1 part in a million are sought. The best method of preparing the bottle for the reception of the sample is to pour in a little strong sulphuric acid, and cause it to flow over the entire inner surface of the bottle, then pour most of it out, and wash the bottle with pure water, continuing to rinse it for some time after the washings have ceased to show a trace of the acid. Then, before collecting the sample, the bottle should be thoroughly rinsed out with some of the same water that is to be analyzed.

In taking a sample from a river or pond, care should be taken to avoid scum or other matter floating on the surface. The bottle should be immersed at some distance from the shore, and held under the water until entirely full. A sample of river water should be taken near the middle of the stream. In examining a city supply, it is best to draw the sample from the street mains, and, in examining the water supplied to a house, the water is drawn from a faucet, in the usual manner. To obtain a fair sample in such cases, the water should be allowed to run a short time before taking the sample, in order to avoid collecting the water that has been standing in the pipes for some time.

In any case, the bottle should be nearly, but not quite, filled with the water; the stopper should be inserted at once, and a piece of clean linen cloth drawn over it tightly and tied in place. It is best to avoid any luting, but if anything of the kind is to be used when a cork stopper is employed, a little sealing wax is probably best, but great care must be taken in opening the bottle in such cases, to prevent any of it getting in the sample. The sample should be kept in a cool dark place, and the examination should take place as soon as convenient after the sample is taken. At all events, the analysis should be made within 48 hours if possible.

TOTAL SOLIDS.

84. The total amount of solid matter in a sample of water was at one time considered a very important indication of its quality, but, at present, it is not regarded as very important, and is frequently omitted. As the determination is very simple, and indications of greater or less value are obtained in this way, it should usually be made. The details of the process are as follows:

85. Determination of Total Solids.—Make a water bath by filling a rather tall beaker to about half its capacity with water, placing it on a gauze over a Bunsen burner, and heating it to boiling. On this, place a perfectly clean platinum dish of convenient size to be weighed (one weighing about 50 grams is a good size), and heat it for a few minutes. Remove it from the water bath, wipe the water from the outside of the dish with a clean dry cloth, place it in a desiccator, and weigh as soon as cool. The dish will cool rapidly; generally, if taken from the water bath, wiped quickly, placed in a desiccator, and taken directly to the balance, it will be cool when it arrives there, and may be weighed at once.

After weighing the dish, place it on the water bath again, and pour into it 100 cubic centimeters of the water to be analyzed. As a rule, the dish employed will not hold this amount, and the water must be added in successive portions. In this case, measure out 100 cubic centimeters of the water, add enough of it to fill the dish to about three-fourths its capacity, and stand the rest aside, keeping it covered to protect it from dust. When about two-thirds of the water in the dish has evaporated, add the remainder, and evaporate to dryness. Leave the dish on the bath 10 or 15 minutes after the residue appears dry, to expel the last traces of moisture; then remove it, wipe the outside with a clean soft cloth, place it in a desiccator, and weigh as soon as cool. As 100 cubic centimeters (.1 liter) of the water was taken for this determination, the weight in milligrams of the residue multiplied by 10 gives the milligrams of total solids in a liter of the water, or, what is the same thing, the parts per million.

Many chemists prefer to stand the dish on a cold, clean porcelain slab to cool, but as the residues from many samples of water contain deliquescent substances, and, therefore, rapidly increase in weight when allowed to stand in the air, it is always best to cool the dish in a desiccator; and, in every case, the dish should be weighed quickly, as soon as it is cold.

86. Examination of the Residue.—Formerly, it was the custom to ignite the residue, weigh again, and call the loss *organic matter*, and the results thus obtained were considered very significant. It is now known that the loss in weight during this operation is, in most cases, principally due to other constituents, and the results thus obtained are utterly valueless as far as their original purpose is concerned. Having the solid residue, however, it is well to make a slight examination of it as follows:

Remove a portion of it to another dish, and add a few drops of hydrochloric acid. If effervescence occurs, it shows the presence of a carbonate, probably of calcium. Pour the solution into a test tube, render it alkaline with ammonia, and see if it remains clear. Then add a few drops of ammonium oxalate, and heat the solution. The formation of a white precipitate shows the presence of calcium, which, taken together with the effervescence, proves that the water contains calcium carbonate, which is found in all the water in limestone districts, and is comparatively harmless.

Cautiously heat the dish containing the remainder of the residue over a Bunsen burner, and note any change in the appearance of the residue, and any odor that may be given off. The heat should be applied very gently at first, and the temperature raised gradually, until the dish becomes red. If the residue becomes dark-colored, organic matter is indicated, and the amount of organic matter present may be roughly surmised from the depth of the color developed. Organic matter, as a rule, also emits an odor when burned, and this should be noted.

The amount of solid matter permissible in a water to be used for domestic purposes depends, of course, on the

character of the solids; hence, this determination taken alone is of but little value in determining the quality of a water. If, however, the residue is examined as directed, something more of the character of the water is indicated, and, when the results of this determination are considered together with those of the other determinations to be made, they help to form an opinion as to the quality of the water. The water may contain considerable mineral matter of a harmless nature and still be a very good water for domestic use. Many very good drinking waters contain as much as 300 or 400 milligrams of total solids per liter, and, unless the sample contains more than 500 milligrams of solid matter, it should not be condemned for domestic use for this reason alone.

CHLORINE.

87. Determination of Chlorine.—In determining the chlorine in water, we avail ourselves of the well known relation between silver, chlorine, and chromic acid. When a solution of silver is added to a solution containing both a chloride and a chromate, the silver unites with the chlorine until it is all precipitated as white silver chloride, and then begins to unite with the chromic acid, forming red silver chromate. The details of the process are as follows:

Measure 100 cubic centimeters of the water into a clean porcelain dish, add a few drops of potassium-chromate solution, and titrate with a standard solution of silver nitrate. As each drop of the silver solution falls into the water, it produces a red color at the point of contact, owing to the fact that all the chlorine in this part of the water is precipitated, and the silver left over unites with chromic acid, forming red silver chromate. On stirring, this precipitate comes in contact with more chlorine, which immediately takes the silver from the chromic acid, and forms white silver chloride, thus destroying the color. This goes on until all the chlorine is precipitated as silver chloride, when an additional drop of silver nitrate will give the solution a permanent reddish color, showing that the reaction is complete. From the

quantity of silver solution used, calculate the amount of chlorine in 100 cubic centimeters of the water. This result multiplied by 10 gives the amount of chlorine in a liter. This amount of chlorine in milligrams is, of course, parts per million.

Some chemists prefer to evaporate 1 liter of the water to a small bulk before titrating, and this is a good plan, in order to check the results, when the water only contains a very little chlorine. It is also a good plan to add more of the potassium-chromate indicator, and then another drop of the silver solution, after the reaction is complete, to see if a marked increase in the red color occurs. Neither of these checks can be considered essential, however, for the writer has repeatedly checked analyses without obtaining results that differed appreciably.

88. Significance of Chlorine.—Chlorine generally exists in water combined with sodium in the form of common salt, and, as this is an article that we require, and take into the system daily, it matters little whether it is taken with our food or in the water we drink; hence, chlorine in itself, unless the amount is excessive, is no cause for rejecting a water for domestic use. Probably too much stress has been laid on the determination of chlorine in drinking water; and water that was organically pure, and of very good quality for domestic use, has been rejected on account of the chlorine it contained. This is an important determination, however, when the results are considered in connection with those obtained in the other determinations, and are intelligently interpreted. A little consideration of the matter will show how they may be of use. The water in regions remote from salt deposits frequently contains but a mere trace of chlorine, while sewage is always heavily charged with this element; hence, any considerable quantity of chlorine in a water has come to be regarded as an indication of sewage contamination.

A water containing a marked increase in chlorine over the amount usually found in the locality from which the water

comes, should certainly be regarded with suspicion. This determination is important in the examination of samples of water suspected of sewage contamination during an epidemic, on account of the rapidity with which results may be obtained. In such cases, if a water is found to contain a considerable quantity of chlorine, its use should be suspended at once, pending a further examination. It must always be borne in mind that a water may be heavily charged with organic matter of vegetable origin, and still contain but very little chlorine, and, consequently, freedom from chlorine is no sign that water is free from organic matter of vegetable origin, and this is, of course, to be avoided. Sewage contamination is regarded as more dangerous than the same amount of vegetable matter, and the amount of chlorine in a water may help us to decide whether the contamination is of animal or vegetable origin, and may thus help us to discover the source of pollution.

It is impossible to say how much chlorine a water may contain without being suspected of sewage contamination, for the normal quantity of chlorine varies greatly in different sections of the country; but when the normal quantity in any locality has been established, any increase over this amount should be regarded with suspicion. The writer has analyzed samples of water containing less than 1 part per million of chlorine, while near the coast or in the vicinity of salt deposits, water that is perfectly wholesome may contain more than 20 parts per million of this element.

SOLUTIONS FOR CHLORINE DETERMINATION.

89. Silver Nitrate.—The silver-nitrate solution for this purpose is usually made of such strength that 1 cubic centimeter of it will precipitate exactly 1 milligram of chlorine. It is made up as follows: Weigh out exactly 4.7943 grams of the pure, dry silver-nitrate crystals; transfer this to a graduated liter flask, dissolve it in pure distilled water, and dilute the solution to exactly 1 liter. As silver nitrate is weighable, this solution will be of such strength that 1 cubic

centimeter of it will precipitate exactly 1 milligram of chlorine, if the pure salt is used, but it is best to check it by running it against a sodium-chloride solution of known strength. To make this solution, dissolve 1.6502 grams of pure, dry sodium chloride in water, dilute to 1 liter, and mix thoroughly, using distilled water that is free from chlorine, of course. Each cubic centimeter of this solution contains exactly 1 milligram of chlorine, and, therefore, should exactly match the silver solution. This solution is sometimes handy in making the determinations. After taking the burette reading when titrating, a few more drops of the silver solution may be added, to produce a deep-red color; this may be destroyed with a measured quantity of the salt solution, and silver nitrate again added until the reaction is complete. Then, by subtracting the amount of sodium chloride added from the total quantity of silver nitrate used, a check on the determination is obtained.

90. Potassium Chromate.—The solution of potassium chromate used as indicator is usually a cold saturated solution of the pure salt in pure water. The solution may be made up by dissolving about 20 grams of the pure salt in 100 cubic centimeters of water. Both the potassium chromate and the water used in making up this solution must be absolutely free from chlorine. Of course, this applies with equal force to the materials used in making up the other solutions for this determination.

THE AMMONIA PROCESS.

91. The determination of total solids and chlorine gives us indications that are valuable in throwing light on the subject when considered in connection with other results, but are of little value in themselves. We now come to the determination of organic matter, and the results obtained are usually sufficient in themselves to establish the character of the water. The ammonia process is divided into two parts, the determination of *free ammonia* and of *albuminoid*

ammonia. The process depends on the fact that when a sample of water is boiled with sodium carbonate, the free ammonia (which term includes ammonium salts) dissolved in it is expelled, and passes off with the first part of the water as it is evaporated. Now, having the water free of uncombined ammonia and ammonium salts, if potassium permanganate and a large excess of potassium hydrate are added and the boiling continued, the nitrogenous organic matter is decomposed, yielding a quantity of ammonia proportional to the amount of such matter contained in the water. The ammonia is collected in the distillate, and its quantity determined by means of the very delicate Nessler reagent. The determination of the ammonia is one of the most important, if not the most important, of the determinations made in the examination of water for domestic use. The details of the process are as follows:

92. Free Ammonia.—Choose a tubulated retort that will hold from 1.5 to 2 liters, and provided with a ground-glass stopper; cleanse it thoroughly by rinsing it out, first

FIG. 15.

with strong sulphuric acid, and then washing until the washings contain no acid, finally with distilled water, and fix it in the clamp on a retort stand, as shown at *a*, Fig. 15. Fit

the neck of the retort into the tube of a Liebig condenser, wind it tightly with a piece of thin flexible rubber, and bind this in place by means of a cord, as shown at *b*, thus securing a perfectly tight connection. Under the end of the condenser tube, stand the Nessler cylinder *c* to collect the distillate. From half a dozen to a dozen Nessler tubes will be required for the determination. They should be made of thin colorless glass, and must be of uniform size and form. Cylinders of a little more than 100 cubic centimeters capacity are probably the most convenient; each should have a mark on the side to show when 50 cubic centimeters of distillate have been collected, and they should be so nearly of the same size that these marks will all come within one-sixteenth of an inch of one another. The bottoms of the tubes should be perfectly flat, so that they will stand firmly on the working bench or table. The arrangement of the apparatus will be understood from Fig. 15.

When all is in readiness, measure 200 cubic centimeters of absolute water into the retort, add 10 cubic centimeters of sodium-carbonate solution, drop in five or six small glass balls, to prevent bumping, and close the retort with the ground-glass stopper, which must be scrupulously clean. Place a good Bunsen burner under the retort, so that the flame plays directly on it, but take care not to allow the flame to strike the glass above the water line. When 50 cubic centimeters of distillate have passed over, remove the Nessler cylinder, and place a clean one in its place, to collect the next 50 cubic centimeters of distillate passing over. When 100 cubic centimeters have passed over, remove the light from the retort. This will remove any ammonia that remained in the retort, or that may have been introduced with the sodium carbonate, and the 100 cubic centimeters of water and sodium carbonate, as well as the retort itself, are now perfectly free from ammonia. It is well to test the two distillates collected, with Nessler reagent, to learn if there was any ammonia to start with.

Now measure 500 cubic centimeters of the water to be examined into the retort, stopper it tightly, return the

burner to its position, and so regulate the flame that about 50 cubic centimeters of distillate will collect every 15 minutes. If the distillation is carried on much more rapidly than this, some ammonia will escape. While the first 50 cubic centimeters of distillate are collecting, measure different quantities of standard ammonia solution into several Nessler cylinders, and dilute each to 50 cubic centimeters with absolute water. It is handy to have such standards ranging from .005 to .05 milligram of ammonia in the 50 cubic centimeters of water. When the first cylinder is filled to the 50-cubic-centimeter mark, remove it, and stand a clean cylinder in its place, to collect the next 50 cubic centimeters of distillate passing over. By means of a 2-cubic-centimeter pipette, drop exactly 2 cubic centimeters of Nessler reagent into each of the standards and the 50 cubic centimeters of distillate, and stir each up. The Nessler reagent will almost immediately impart to each a reddish-brown color, the depth of which depends on the amount of ammonia it contains. Have the cylinders standing on a white surface, and, by looking down through them, compare the colors and match the sample with a standard. If the sample has a color differing from that of any of the standards, a very close estimate of the amount of ammonia it contains may be made. In this case, quickly make up two more standards containing very nearly the estimated amount of ammonia, add 2 cubic centimeters of Nessler reagent to each, and, after allowing them to stand about 1 minute, compare the sample with these standards.

These standards must be made up quickly, for on standing a few moments after the Nessler reagent is added, the colors begin to change quite rapidly. When a standard is obtained, the color of which exactly matches that of the distillate, we know that each contains the same quantity of ammonia, and as the amount of ammonia in the standard is known, we thus learn the quantity in the distillate. If the distillate contains more ammonia than any of the standards, it may be diluted to 100 cubic centimeters, stirred well, half of the solution poured out, 1 cubic centimeter of Nessler

reagent added to the portion remaining in the tube to make the quantity of Nessler reagent in each tube the same, and the colors again compared. But under no circumstances must ammonia be added to a solution after the Nessler reagent has been added, for this is almost certain to give erroneous results. The free ammonia will frequently all pass over in the first three portions of distillate, and it is very seldom that any remains after the fourth, but, for the sake of uniformity, five portions of distillate, of 50 cubic centimeters each, should always be collected and Nesslerized, just as was done with the first portion. By adding the results obtained in Nesslerizing the five portions of distillate, the amount of free ammonia in 500 cubic centimeters of the water is obtained, and the result thus obtained in milligrams, multiplied by 2, gives the number of parts of free ammonia in a million parts of water.

93. Albuminoid Ammonia.—The free and the albuminoid ammonia are determined in the same sample. When 250 cubic centimeters of the water have passed over and been Nesslerized for free ammonia, remove the burner for a few moments, add 50 cubic centimeters of a solution of potassium hydrate and potassium permanganate, return the burner to its place, and continue the distillation. Collect the distillate in portions of 50 cubic centimeters each, and Nesslerize just as in the determination of free ammonia, continuing the operation as long as a distillate gives a reaction with Nessler reagent. The total amount of ammonia found in this way after the potassium hydrate and permanganate solution is added, is the albuminoid ammonia formed by the decomposition of the nitrogenous organic matter in 500 cubic centimeters of the water, and this amount in milligrams, multiplied by 2, gives the albuminoid ammonia in the water in terms of milligrams per liter or parts per million.

In laboratories where many water analyses are made, the very handy form of apparatus shown in Fig. 16 is largely used for this process. The flask *a* has a capacity of about 2 liters; it is provided with a ground-glass stopper that fits

perfectly, and has a side neck tube that is bent to point straight downwards when the flask is held in the clamp *b* over the burner *c*. The side neck tube is connected with the zigzag tube passing through the vertical condenser *d*, and the Nessler cylinders are held in the rack *e* in such a way that they pass successively under the zigzag tube to receive the

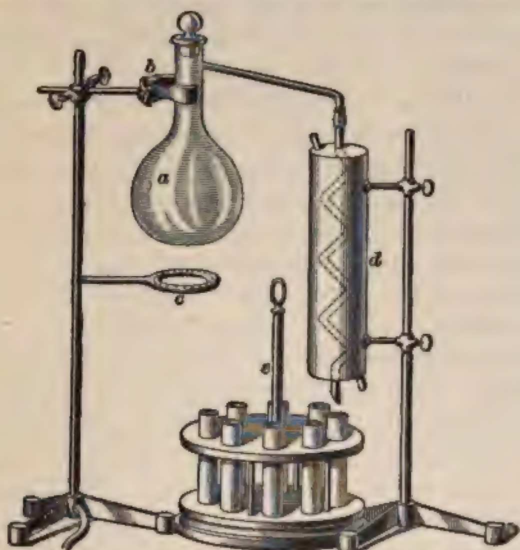


FIG. 16.

distillate when the rack is revolved. When using this apparatus, measure the sample into the flask *a*, insert the stopper tightly, light the burner *c*, and proceed with the determination exactly as when a retort is used.

94. Significance of Ammonia.—Nearly all natural waters contain minute quantities of free ammonia, and this in itself is not injurious; but an increase in the amount of this constituent points to unhealthy conditions. It has been suggested that free ammonia is produced in water by the breaking up of albuminous matter before the water is examined, thus indicating that the water is undergoing purification, but that it is not yet sufficiently pure for

domestic use. Water that is contaminated with urine yields a relatively large amount of free ammonia. For this reason, it is sometimes spoken of as *ureal* ammonia, and is regarded as an indication that the water is polluted with sewage. It is the writer's experience, however, that free ammonia sometimes comes from other sources. The amount of free ammonia in water varies with the source. It is usually greater in wells than in streams or ponds. Chemists differ as to the amount that may be present without danger to health. It may be stated, however, that water containing more than .1 part per million should never be used, and, to be considered as very pure, it should contain considerably less than this, especially if coming from a stream or pond.

Although chemists differ somewhat in regard to the significance of free ammonia, they all agree that a relatively large amount of albuminoid ammonia indicates a very dangerous condition, and that a water yielding a very large amount of this constituent should be condemned without qualification. The albuminous matter in water may be either of animal or vegetable origin. The former is regarded as the most dangerous, but the latter, if present in excessive quantity, is almost certain to cause disease. If familiar with the surroundings, the character of the organic matter in a sample of water may be inferred from its source. Another indication is obtained when the water is distilled in the determination of ammonia. The albuminoid ammonia derived from animal matter usually comes over more rapidly and regularly than that from vegetable matter. Much may also be inferred from the results of the other determinations. Water containing vegetable matter alone is frequently almost free from chlorine and free ammonia, while the albuminoid ammonia is relatively high. On the other hand, water polluted with sewage always contains an increased amount of chlorine, and, generally, free ammonia also. Wanklyn, who devised this process, says that the albuminoid ammonia should never exceed .15 part per million, and this limit undoubtedly holds in the case of wells and other waters that may contain sewage contamination.

Chemists are at present inclined to allow a little more in the case of streams and ponds in thickly wooded districts, where the organic impurity consists principally of dead leaves; but, in this case, the water should not contain more than .25 part per million of albuminoid ammonia. In any case, it should be remembered that in order to be regarded as very pure, the water should contain considerably less than these figures given as limits.

SOLUTIONS FOR THE AMMONIA PROCESS.

95. Absolute Water.—Ordinary distilled water cannot be used in making the solutions used in the ammonia process, for it contains enough ammonia to render it useless for this purpose, and ammonia-free water, known as absolute water, must be prepared. The best way to do this, is to make use of the fact that when water is distilled, the free ammonia all passes over with the first third of the distillate, the second third of the distillate is free from ammonia, and the last third contains the remainder of the ammonia. Place a convenient quantity—say 15 liters—of good drinking water in a distilling apparatus and apply heat. Discard the first 5 liters of distillate, then test a little of the distillate with Nessler reagent, and, if it is free from ammonia, collect the next 5 liters, and then stop the distillation. The portion collected will be free from ammonia, and is known as absolute water. The first portion passing over should not be thrown away, as it is sufficiently pure for ordinary use as distilled water. The portion remaining in the distilling apparatus should be thrown out, however, and the apparatus should be rinsed out with fresh water. The absolute water should be kept in glass-stoppered bottles, and it is best to cover the tips with caps to prevent the deposition on them of ammonium compounds from the air of the laboratory. It should be used within a reasonable time after it is prepared, for after standing a long time in the bottles, it will give a cloudy solution when Nessler reagent is added, and is therefore useless for this purpose.

96. Sodium Carbonate.—This solution is made by dissolving 50 grams of pure sodium carbonate in 250 cubic centimeters of absolute water. It should be kept in a bottle with a ground-glass stopper, but care must be taken to keep the stopper from sticking. The object of the solution is to expel any so called free ammonia that is combined with an acid. Its use would not be necessary in many cases, but, for the sake of uniformity, it should be added to every sample. It may be stated here that perfect uniformity of conditions is essential for success in water analysis.

97. Nessler Reagent.—Dissolve 15 grams of mercuric chloride in about 500 cubic centimeters of absolute water. Dissolve 35 grams of potassium iodide in about 200 cubic centimeters of absolute water. Pour the first solution into the second, until a faint, permanent, red precipitate begins to form, adding the mercuric chloride cautiously towards the last. The solution at this point should contain a very slight red precipitate that does not redissolve, even upon vigorous stirring. It now remains to make it strongly alkaline, and to render it sensitive. To do this, add 160 grams of pure solid potassium hydrate, and when it has dissolved and the solution has cooled, dilute it to 1 liter with absolute water, and mix it thoroughly. If potassium hydrate is not at hand, 120 grams of pure sodium hydrate may be substituted for it. The slight reddish precipitate in the solution will be dissolved by the potassium hydrate, and more mercuric chloride must now be added to render the solution sensitive. A cold saturated solution in absolute water is used. Add it cautiously until the last drop added produces a permanent precipitate, and allow this to settle. The clear supernatant liquid should now have a slight yellowish tint, and, if colorless, it is never sensitive. In this case, a little more mercuric chloride must be added, and, after being thoroughly mixed, the solution must be allowed to settle again.

The solution should next be tested to ascertain its condition. For this purpose, measure a quantity of the dilute standard

ammonia solution, containing .01 milligram of ammonia, into a Nessler cylinder; dilute it to 50 cubic centimeters with absolute water, and add 2 cubic centimeters of the solution to be tested. If it is sufficiently sensitive, a yellowish-brown tint will be imparted to the solution in the Nessler cylinder almost immediately. If a distinct color is not developed in the course of half a minute, the solution is not sufficiently sensitive. In this case, add more mercuric chloride, mix thoroughly, allow it to settle, and test again. The stock of Nessler reagent should be kept in a tightly stoppered bottle, and, from time to time, small quantities of it are poured into a small bottle, from which it is drawn as it is used.

98. Standard Solution of Ammonia.—A dilute solution of ammonium chloride is used as a standard in Nesslerizing. It is made up as follows: Dissolve 3.14 grams of pure ammonium chloride in absolute water, dilute to exactly 1 liter with absolute water, and mix the solution thoroughly. This solution is of such strength that 1 cubic centimeter of it contains 1 milligram of ammonia NH_3, and is therefore much too strong for use in Nesslerizing. By means of a burette, measure exactly 10 cubic centimeters of this solution into a liter flask, dilute it to the mark with absolute water, and mix it thoroughly. This solution contains .01 milligram of ammonia in 1 cubic centimeter, and is therefore of a convenient strength to use in Nesslerizing. This solution should be kept in a glass-stoppered bottle, the lip of which is protected from ammonium compounds in the air by means of a cap. In examining extremely bad waters, it is sometimes handy to have a stronger standard solution of ammonia. Such a solution is made by diluting 100 cubic centimeters of the strong solution first made up to 1 liter. This solution will be of such strength that 1 cubic centimeter of it contains .1 milligram of ammonia.

99. Potassium Hydrate and Permanganate.—This solution, which is used to decompose the nitrogenous organic

matter, and set free the albuminoid ammonia, is made as follows: Dissolve 8 grams of pure crystallized potassium permanganate and 200 grams of potassium hydrate in 1 liter of distilled water. Boil the solution until about one-fifth of it has evaporated, and add sufficient absolute water to bring the volume of the solution up to 1 liter when it is cold. Keep the solution in a glass-stoppered bottle, and, when not using it, move the stopper every few days, to keep it from sticking. This solution must always have the reddish-violet color of permanganate. If it becomes green, either in the stock bottle or in the retort when in use, no reliable results can be obtained with it, and a fresh solution must be made up.

100. Practical Suggestions.—If many analyses of water are made, it is best to set apart a portion of the laboratory for this purpose exclusively, and to keep it as free from fumes as possible. The ammonia process cannot be carried out successfully in a laboratory filled with ammonia fumes. It is best to keep the apparatus used in the ammonia process for that purpose alone. At all events, it should not come in contact with organic matter. The apparatus must be thoroughly cleaned before it is used. It is not sufficient to clean it before putting it away, and then to use it without a second washing, for ammonium compounds from the air may be deposited in sufficient quantity to vitiate the results. It is not usually necessary to employ distilled water in washing the apparatus. If washed with a large quantity of good tap water and allowed to drain, it will be perfectly clean; and, under no circumstances, should apparatus used in water analysis be wiped with a cloth.

THE MOIST COMBUSTION PROCESS.

101. Before the ammonia process came into general use, chemists tried to estimate the amount of organic matter in water by the amount of oxygen required to oxidize it, using potassium permanganate to supply the oxygen. The methods employed were rather crude, and the results obtained were

unsatisfactory, as, in many cases, only a small fraction of the organic matter was oxidized. At present, the so called moist combustion process is largely used, and it is believed that by this method the organic matter in a water is oxidized, and the amount of oxygen used may be accurately measured. It has been objected to this process that when two samples are treated, one of which contains vegetable matter, and the other an equal amount of animal matter, the water containing the vegetable matter will consume the larger quantity of oxygen, while that containing the animal matter is undoubtedly the more dangerous.

While the results obtained by this method are probably not so important as those obtained by the ammonia process, they are of value inasmuch as they give a further idea of the amount of organic matter in a sample, and also of its character. It has been stated that the weight of organic matter in a liter of water is approximately equal to the weight of oxygen consumed when a liter of the water is subjected to the moist combustion process. While this statement is correct when the organic matter is starch and some other compounds, it will not hold good in all cases, and, consequently, the results should be stated in milligrams of oxygen consumed, without attempting to state the weight of organic matter present.

The amount of oxygen that may be consumed by the carbonaceous matter in a liter of water without rejecting it for domestic use, is not so clearly defined as in the case of ammonia. In fact, the results obtained by this process are more largely used to throw light on the results of the ammonia process than to establish the quality of the water, when considered by themselves. It may be stated, however, that to be considered of first-class quality, a liter of the water should not consume much more than .5 milligram of oxygen. Many drinking waters that are considered wholesome consume from 1 to 2 parts of oxygen per million, but anything above this should be regarded with suspicion, and a water, 1 liter of which consumes more than 3 milligrams of oxygen, should usually be rejected. The details of the process are as follows:

102. Determination of Oxygen Consumed.—Clean a retort thoroughly by washing it with a large quantity of water, allow it to drain, and mount it on a retort stand just as in the determination of ammonia. The retort used for the ammonia process may be employed for this purpose also, but it is best to have two similar retorts and keep each for its own purpose. After cleaning and mounting the retort, introduce exactly 1 liter of the water to be tested, 5 cubic centimeters of potassium-hydrate solution, and 5 cubic centimeters of potassium permanganate, 1 cubic centimeter of which contains 1 milligram of available oxygen. As this solution is likely to bump towards the end of the distillation, especially if the water is bad, a few glass balls should be introduced, as in the case of the ammonia process, to prevent bumping. Place a good Bunsen burner so that the flame plays directly on the retort, and distil over about 900 cubic centimeters of the water, thus leaving about 100 cubic centimeters in the retort. The water should retain a distinct pink color throughout the distillation. In the case of very impure water, the permanganate added may not be sufficient to oxidize all the carbon, and the color will be destroyed before the operation is complete. In such cases, the burner must be removed, and 5 cubic centimeters more of the permanganate added, while the color of the solution is still distinctly pink.

When about 900 cubic centimeters of the water have passed over, remove the burner, add 10 cubic centimeters of the sulphuric-acid solution, then 5 cubic centimeters of standard ferrous solution, that exactly matches the permanganate, and agitate the contents of the retort. The ferrous solution will rapidly decolorize the remaining permanganate. As soon as this is accomplished, pour the solution into a beaker or porcelain dish, wash out the retort with about 200 cubic centimeters of cold distilled water, adding the washings to the main solution, and titrate at once with the standard permanganate. As the 5 cubic centimeters of ferrous solution added to the retort would exactly reduce the permanganate added at the beginning of the operation, if none of it had been

reduced by organic matter, the quantity of permanganate added in titrating the solution at the end of the operation is equal to the amount of permanganate destroyed in oxidizing organic matter. Or, in other words, the total amount of permanganate used, minus the quantity consumed by the ferrous solution, equals the quantity of permanganate consumed in oxidizing the organic matter; and, as each cubic centimeter of the permanganate contains 1 milligram of available oxygen, the result thus obtained in cubic centimeters represents the milligrams of oxygen consumed by the organic matter in a liter of the water. The permanganate and the ferrous solutions should be measured into the retort by means of a burette, and the exact quantities added should be noted. The exact quantity of each added is not a matter of great importance so long as enough ferrous solution is added to completely decolorize the permanganate remaining in the retort at the end of the operation, and the exact amount of each that is added is known; but it is handy, and has become customary, to add exactly 5 cubic centimeters of each before the titration.

SOLUTIONS FOR THE MOIST COMBUSTION PROCESS.

103. Ferrous Solution.—As ferrous ammonium sulphate is the most stable of the common ferrous salts, it is the best one to use in making the ferrous solution. This solution is made of such strength that it will exactly match a permanganate solution, each cubic centimeter of which contains 1 milligram of available oxygen. By considering the relations of potassium permanganate, oxygen, and ferrous ammonium sulphate, the method of calculating the amount of ferrous ammonium sulphate necessary to make a liter of such a solution becomes apparent. We have seen that 2 molecules of potassium permanganate $KMnO_4$, which contain 5 atoms of available oxygen, oxidize 10 molecules of ferrous ammonium sulphate. Hence, ten times the molecular weight of ferrous ammonium sulphate (3,924) divided by five times the atomic weight of oxygen (80) gives 49.05 grams, the weight

of ferrous ammonium sulphate necessary to make 1 liter of the required solution. It is made up as follows: Weigh out 49.05 grams of small crystals of pure ferrous ammonium sulphate, that have not lost water of crystallization, and transfer them to a liter flask. Add about 500 cubic centimeters of water, then 50 cubic centimeters of concentrate sulphuric acid, agitate the contents of the flask until solution is complete; when cool, dilute exactly to the liter mark with pure water, and mix the solution as well as possible in the flask. Transfer the solution to a clean, dry glass-stoppered bottle that it will almost fill, and shake it well to secure thorough mixing. The bottle used to contain this solution must have a perfectly tight stopper, and should be kept in a cool dark place. Even under the most favorable conditions, it gradually changes in strength, and must be restandardized at frequent intervals.

104. Potassium Permanganate.—The permanganate solution, as we have seen, is made of such strength that 1 cubic centimeter of it contains exactly 1 milligram of available oxygen. To have this strength, a liter of the solution must contain 3.9525 grams of potassium permanganate, and 1 cubic centimeter of it will oxidize exactly 1 cubic centimeter of the ferrous solution. To make this solution, dissolve about 4 grams of potassium permanganate in a liter of water and mix the solution thoroughly. After allowing it to stand for 24 hours, measure 20 cubic centimeters of the ferrous solution from a burette into a beaker or porcelain dish, dilute to about 200 cubic centimeters, add 5 cubic centimeters of dilute sulphuric acid, and titrate with the permanganate solution. From the amount of permanganate required to produce a faint permanent pink tinge, calculate how much water must be added and dilute the permanganate until the solutions are exactly matched. The permanganate will now be of the proper strength for use.

105. Potassium Hydrate.—Different writers recommend slightly different strengths for this solution, and the

exact strength is not a matter of great importance. A solution of approximately normal strength is handy, and serves well for the purpose. It is made by dissolving 56 grams of the solid in about 600 cubic centimeters of water and diluting to 1 liter.

106. Sulphuric Acid.—Like the potassium hydrate, this solution is made of different strengths. Wanklyn recommends a solution made by adding 100 cubic centimeters of concentrate sulphuric acid to 1 liter of water, and some chemists recommend a solution containing as little as 30 cubic centimeters of concentrate acid to the liter. A very good solution for the purpose is made by adding 50 cubic centimeters of concentrate acid to 700 or 800 cubic centimeters of water, and diluting to 1 liter after it has cooled.

NITROGEN AS NITRITE.

107. Some chemists assert that the presence of nitrous acid or its salts in water may be due to thunder storms or electrical disturbances in the atmosphere, and, consequently, conclude that its presence does not necessarily indicate impurity. Others, on the other hand, believe that the purest water is always free from nitrous acid, and regard its pressence in any considerable quantity as a very bad indication under any circumstances. Probably neither view is entirely correct. Whatever may be the case in rare instances, it is now generally admitted that nitrites found in pond or river water ordinarily come from the putrefaction of nitrogenous organic matter—usually of animal matter. In deep wells, the conditions are somewhat different. These waters may contain nitrites that have been formed by the deoxidation of nitrates in percolating through strata containing mineral reducing agents.

The importance attached to this determination by different chemists depends on the opinion they hold as to the origin of nitrites in water. Professor Mallet considers this determination of great importance, and the writer's experience

agrees perfectly with this view. At all events, the result of this determination should be kept in mind in deciding the quality of a water, and, when nitrites are present, the results of the other determinations should be interpreted with greater strictness than when they are absent. As chemists differ as to the significance of nitrous acid in water, they naturally differ as to the amount that may be present without danger. Professor Mallet examined eighteen samples of water from different sources, all of which were believed to be wholesome, and found that the average of the eighteen samples was .0135 part of nitrogen as nitrite in a million parts of water. He also examined nineteen samples of waters that were thought to have caused disease, and found the average to be .0403 part of nitrogen as nitrite per million. It has been the writer's experience that the nitrogen as nitrite found in good wholesome water is usually much less than the figures given above.

The naphthyl-amine test is the most delicate, and, in many cases, the most satisfactory method of determining nitrites in water. It is performed as follows:

108. The Naphthyl-Amine Test.—Take five Nessler tubes, measure into them .5, 1, 2, 3, and 4 cubic centimeters, respectively, of standard nitrite solution, and dilute each to 100 cubic centimeters with absolute water. Then, into a similar Nessler cylinder, measure 100 cubic centimeters of the water to be tested. To each of the standards, and to the sample under examination, add 5 cubic centimeters of the naphthyl-amine solution, mix thoroughly, cover each cylinder with a watch glass, and allow them to stand 20 minutes. At the end of this time, the colors will be fully developed. By looking down through the tubes, the colors are compared, and, by matching the sample with a standard, the quantity of nitrogen existing as nitrite is obtained.

This is an extremely delicate test. It is said to reveal the presence of nitrite in a water containing only .001 milligram of nitrogen as nitrite in a liter. The color, which is

similar to that of a dilute permanganate solution, is developed more rapidly if the solutions are heated to 70° or 80°; but, as a color is likely to be produced in this case by nitrites contained in the products of combustion, it is best to allow them to stand covered for 20 minutes at the temperature of the room. It has been objected to this method that it is too delicate for quantitative use with water containing a relatively large amount of nitrite, and, for such water, some chemists prefer the following method:

109. Griess's Method.—Measure 100 cubic centimeters of the water to be tested into a Nessler cylinder; add 1 cubic centimeter each of one-third strength sulphuric acid and metaphenylene diamine, and mix the solution. If the color forms at once, a smaller portion of water must be taken, and diluted to 100 cubic centimeters with absolute water. When a distinct color just begins to appear in from half a minute to a minute, the proper degree of dilution is indicated. Now measure the quantity of water indicated by the test into a Nessler cylinder, and dilute it to 100 cubic centimeters; then make up several standard nitrite solutions just as in the naphthyl-amine test. To each cylinder, add 1 cubic centimeter each of one-third strength sulphuric acid and metaphenylene diamine, mix well, cover each cylinder with a watch glass, and allow them to stand 20 minutes. By looking down through the solutions in the Nessler cylinders, compare the colors, and thus determine the amount of nitrogen as nitrite in the quantity of water taken. As this quantity is known, the amount of nitrogen in a liter of the water is readily calculated.

In using the naphthyl-amine test, if the water contains a relatively large amount of nitrite, a smaller sample of it may be diluted to 100 cubic centimeters, and tested as in the case of Griess's method. And in using either method, if the Nessler cylinders at hand do not readily contain 100 cubic centimeters, 50 cubic centimeters each of sample and standards may be used almost equally as well.

SOLUTIONS FOR NITROGEN AS NITRITE.

110. Naphthyl-Amine Solution.—Boil .1 gram of α-naphthyl amine in 20 cubic centimeters of water, pour off the clear solution, and mix it with 150 cubic centimeters of acetic acid of 1.04 Sp. Gr.—about 30 per cent. Then dissolve .5 gram of sulphanilic acid in 150 cubic centimeters of acetic acid of the same strength as that used with the naphthyl amine, mix the two solutions, and keep them in a tightly stoppered bottle. If a color is developed when these solutions are mixed, the reagent may be decolorized by shaking it up with powdered zinc and filtering into a clean bottle. A few drops of sulphuric acid may be added with the zinc if necessary. The solution is not affected to any considerable extent by light, but must be protected from the air. Some chemists prefer to keep the two solutions in separate bottles, and mix a small portion just before using it, but it is handier to have a single solution, even if it has to be made up more frequently. When this reagent acts on a nitrite in dilute solution, a pink color, similar to that of a dilute permanganate solution, is produced.

111. Metaphenylene-Diamine Solution.—This solution is made by dissolving 1 gram of metaphenylene diamine in 200 cubic centimeters of very dilute sulphuric acid, which, of course, must be free from nitrous acid. If the solution is strongly colored, it may be bleached by filtering through pure animal charcoal. When this solution is added to a dilute solution of a nitrite, a brown color is produced owing to the formation of the substance known as *Bismarck brown.*

112. Standard Nitrite Solution.—The sodium or potassium nitrite sold by chemical dealers is not pure enough to be used for this purpose, and, consequently, silver nitrite is employed in its preparation. This salt may be obtained from dealers, but, in order to be sure of its purity, it is best to prepare it. This is done as follows: Make up strong

solutions of silver nitrate and sodium or potassium nitrite, using a very little more of the nitrite than the calculation would indicate as necessary. Heat both solutions just to the boiling point, mix them, and filter at once. The silver nitrite formed dissolves quite readily in boiling water, but crystallizes from the filtrate as it cools. When quite cold, pour off the mother liquor, wash the crystals once by decantation with a little cold water, dissolve them in a little boiling water, filter and recrystallize. Wash these crystals once by decantation with a little cold water, drain this off and dry them, at first over a water bath, and, finally, in a desiccator. When dry, the crystals will consist of pure silver nitrite, 11 grams of which contain 1 gram of nitrogen. The salt must not be exposed to a strong light, either during, or after preparation. Continued boiling must also be avoided, as this tends to slowly decompose the silver nitrite with the formation of nitrate.

Weigh out .275 gram of the pure silver nitrite, dissolve it in a little hot water, and add a slight excess of sodium-chloride solution. This will precipitate the silver as chloride, and form a corresponding amount of sodium nitrite. Filter off the silver chloride, wash the precipitate with absolute water until the filtrate and washings amount to exactly 250 cubic centimeters, and mix this solution thoroughly. Measure out exactly 10 cubic centimeters of this solution, dilute it to 1 liter, mix it thoroughly, and keep it in a tightly stoppered bottle. The liter of solution contains 1 milligram of nitrogen in the form of nitrite, and, consequently, each cubic centimeter contains .001 milligram of nitrogen.

In comparing the colors, if 100 cubic centimeters of the water are taken, and its color is found to match that of the solution in the cylinder containing 3 cubic centimeters of the standard nitrite solution, it shows that 100 cubic centimeters of the water contain .003 milligram of nitrogen, and that 1 liter contains .03 milligram of nitrogen as nitrite. Or, as it is more frequently stated, the water contains .03 part per million of nitrogen as nitrite.

NITROGEN AS NITRATE.

113. The nitrates in water are generally believed to come principally from the oxidation of nitrogenous organic matter, and it has been asserted that when the nitrogen reaches this state of oxidation, all danger is past, and the nitrates can only be considered as an evidence of past pollution. Experience does not support this statement, for water containing 5 parts per million of nitrogen as nitrate, though the albuminoid ammonia was low, has been known to cause disease. The amount of nitrogen in the form of nitrate ordinarily present in a water, depends on its source. In ponds and streams, the quantity is generally rather less than .2 part per million, while in wells, it sometimes reaches ten times this figure. Sanitary chemists differ in regard to the amount of nitrogen as nitrate that may be present in a wholesome water, but it is probably safe to say that a well water containing over 3 parts per million should be regarded with suspicion, and that ponds and streams should contain much less than this. There are a number of methods for the determination of nitrogen existing as nitrate in water. The two methods most frequently used are here given.

114. Estimation as Ammonia.—When zinc is placed in a dilute solution of copper sulphate, it is covered with a black firmly adhering deposit of metallic copper. This combination of the two metals is known as the *zinc-copper couple*, and has the power of decomposing water at ordinary temperature. The zinc-copper couple has the power of producing other decompositions that zinc alone cannot. Among these is the reduction of nitric to nitrous acid, and, finally, to ammonia. When the zinc-copper couple is placed in a solution of a nitrate, electrolysis commences; hydrogen is set free, and is occluded by the copper; and oxygen unites with the zinc, forming zinc oxide. The occluded hydrogen acts on the nitrate in its vicinity, reducing it to nitrite, and finally reduces the nitrous acid to ammonia. This action is made use of in the estimation of nitrates as follows:

Nearly fill a glass-stoppered bottle, having a capacity of

300 or 400 cubic centimeters, with pure zinc turnings cut in curls so that they occupy much space and leave large interstices, placing the turnings in the bottle so that they will not fall out when it is inverted. Now fill the bottle with a solution of copper sulphate containing about 3 per cent. of the crystals, and allow it to stand until the zinc is uniformly coated with a copious, black, firmly adhering deposit. The copper-sulphate solution should not contain much more than 3 per cent. of the crystallized salt, and should not be allowed to stand in contact with the zinc too long, or a spongy deposit that will not adhere well may be formed. When about the right amount of copper has deposited, pour out the remaining solution, wash the bottle and contents several times with distilled water, and, finally, with some of the water under examination, pouring the washings over the stopper in each case. The zinc-copper couple is now in proper condition for use.

Cover the couple with the water to be tested, add from .1 to .2 gram of pure oxalic-acid crystals to hasten the action, insert the stopper, and stand the bottle aside overnight. If in a hurry for the results, the reducing action may be still further accelerated by slightly raising the temperature. If the bottle is well filled and tightly stoppered, it may be heated to 30° without danger of losing ammonia, but, ordinarily, it is best to let it stand overnight at the temperature of the laboratory. In the morning, remove a little of the water and test qualitatively for nitrites by means of the naphthyl-amine test. If nitrites are present, the reduction is not complete, and the solution must be allowed to stand until all the nitrous acid is converted into ammonia. When naphthyl amine no longer gives a reaction for nitrous acid, remove a small portion of the water, and make a rough side test with Nessler reagent, to ascertain what volume of the water must be taken in order to have rather less than .04 milligram of ammonia. Measure this amount of the water into a Nessler cylinder, dilute it to 50 cubic centimeters with absolute water, and Nesslerize. To do this, place measured amounts of standard ammonia solution in several

Nessler cylinders, dilute each to 50 cubic centimeters with absolute water, add Nessler reagent to each of the standards, and to the sample to be tested, stir each one, and match the color of the sample with a standard. If the sample is not exactly matched by any of the standards, make up two or three standards containing about the amount of ammonia indicated, and Nesslerize a second sample taken from the bottle, comparing the color of the sample with these standards. Let us suppose, for example, that 25 cubic centimeters of sample, when diluted to 50 cubic centimeters with absolute water, gives a color that exactly matches the color of the standard made by diluting 3 cubic centimeters of the standard ammonia to 50 cubic centimeters. As 1 cubic centimeter of the standard ammonia solution contains .01 milligram of ammonia, 3 cubic centimeters contain .03 milligram, and, consequently, 25 cubic centimeters of the water contain .03 milligram of ammonia. Therefore, 1 liter of the water contains .12 milligram of ammonia, which represents the free ammonia contained in the water, together with that formed by the reduction of nitrates and nitrites. From the weight of ammonia thus found in a liter of water, subtract the weight of free ammonia previously determined, and calculate the weight of nitrogen in the remainder. From this weight, subtract the weight of nitrogen existing in nitrites, and the remainder will be the nitrogen existing as nitrate in a liter of the water.

115. The Picric-Acid Test.—The picric-acid, or the phenol-sulphonic, test depends on the fact that when phenol and sulphuric acid are added to a sample of water, the nitric acid in the water converts a corresponding amount of the phenol into picric acid, and, when an excess of ammonia is added to this, a yellow color is produced, the depth of which depends on the amount of picrate present. By comparing this color with that produced when a solution containing a known quantity of nitrate is similarly treated, the amount of nitrogen existing as nitrate in the water is obtained. The details of the process are as follows: Dissolve .7206 gram of

pure potassium nitrate in absolute water, and dilute the solution to exactly 1 liter for a stock standard solution. This solution is then of such a strength that 1 liter contains 100 milligrams of nitrogen, and, consequently, 1 cubic centimeter contains .1 milligram of nitrogen. When ready to make the determination, measure exactly 10 cubic centimeters of the stock solution into a 100-cubic-centimeter flask, dilute it exactly to the mark, and mix it thoroughly. A solution is thus obtained, 1 cubic centimeter of which contains .01 milligram of nitrogen. Measure 10 cubic centimeters of this diluted solution into a small porcelain dish, and into a similar dish measure 10 cubic centimeters of the water to be tested; place them side by side on water baths, and evaporate to apparent dryness. As soon as the residues appear to be dry, or even while they appear slightly moist, remove the dishes from the water baths. Heating after the residue is dry is almost sure to cause inaccuracies, for nitric acid is slowly expelled by the heat, and some nitrate may be absorbed by the residue from the products of combustion if a gas flame is used in heating the water.

While the sample and standard are evaporating to dryness, mix 6 drops of concentrate phenol and 30 drops of concentrate sulphuric acid. Several methods of making up a stock solution of this reagent have been proposed, but it is found that much more satisfactory results are obtained by making up a small quantity of it just before it is used. Add about 10 drops of this solution to each dish, taking care to add the same quantity to each. Then, by means of glass rods, spread this solution around so that it moistens every particle of the residue. Add 1 cubic centimeter of concentrate sulphuric acid to each dish, and warm them for two or three minutes on the water bath. Then remove them, allow them to cool, add 10 cubic centimeters of water to each, stir them up, add 5 cubic centimeters of concentrate ammonia to each, and stir them again, whereupon the color will develop. Rinse the solution from the sample into a Nessler cylinder, dilute it to 50 cubic centimeters, and treat the standard as the colors produced indicate as best.

In many cases it will be sufficient to wash it into a Nessler cylinder, dilute to 100 cubic centimeters, mix well, remove small measured portions to other cylinders, dilute them to 50 cubic centimeters each, and compare the colors with that of the sample. As 10 cubic centimeters of the dilute standard are taken, the 100 cubic centimeters in the Nessler cylinder contains .1 milligram of nitrogen, and 1 cubic centimeter contains .001 milligram. If 9 cubic centimeters of this are required to make a solution that, when diluted to 50 cubic centimeters, matches the color of the standard, it shows that 10 cubic centimeters of the water under examination contain .009 milligram of nitrogen existing in the form of nitrate, and, therefore, 1 liter of the water contains .9 milligram, or the water contains .9 part per million of nitrogen as nitrate. In examining very pure samples of water, it is sometimes necessary to evaporate a larger quantity, in order to get a color that is strong enough for accurate comparison. As much as 50 cubic centimeters is sometimes required.

It has been asserted that this method does not yield accurate results with samples containing much chlorine, and this appears to be true if the reagent is made up in considerable quantity and allowed to stand some time before it is used, and may be true in extreme cases even when a fresh solution is used. We have obtained very accurate results by using a freshly prepared solution even in the presence of a large amount of chlorine, and it is stated by some chemists that when the fresh reagent is employed, chlorine has no effect on the results, even though an excessive amount of it may be present. The nitrogen existing as nitrite does not interfere with this determination, as nitrous acid forms nitrosophenol, which is colorless in dilute solution.

POISONOUS METALS.

116. Probably the poisonous metals most frequently occurring in water are copper, lead, and zinc. They are sometimes found in the natural water in regions where these metals are mined, and some waters have the power of acting

on lead or copper pipes or fixtures, dissolving these metals; or on galvanized iron pipes or vessels, dissolving zinc. Arsenic and chromium, both of which are poisonous, sometimes occur in water, and iron occurs in small quantities in many waters. This latter element, though not generally considered very poisonous, is, nevertheless, very objectionable when present in considerable quantity. When any of these metals are present, they should not be overlooked. For lead, copper, and iron, very simple colorimetric methods may be used.

117. Lead and Copper.—The method generally employed in determining these metals is due to Miller. It consists in comparing the depth of the colors produced by adding ammonium sulphide to the sample and to a standard solution. The details of the process are as follows: Make up a standard solution of lead nitrate by dissolving 1.599 grams of the pure salt in water and diluting to exactly 1 liter. Each cubic centimeter of this solution will contain 1 milligram of metallic lead. Now measure 100 cubic centimeters of the water to be tested into a Nessler cylinder, add 5 drops of concentrate hydrochloric acid, then 1 cubic centimeter of colorless ammonium sulphide, and stir the solution. Into a similar cylinder, measure a small quantity of the standard lead solution, dilute to 100 cubic centimeters, add 5 drops of concentrate hydrochloric acid, 1 cubic centimeter of colorless ammonium sulphide, stir well, and compare the color produced with that of the sample. Prepare other standards in the same way until one is obtained, the color of which exactly matches the sample. The minute quantity of copper or lead usually contained in water contaminated with these metals, will give the sample a brownish color, due to the formation of the dark sulphide. If the water is rendered alkaline by the addition of the ammonium sulphide, the color may be due to iron; hence, after the color has been obtained, the sample and standard should be rendered distinctly acid with dilute hydrochloric acid, adding the same amount of acid to each. A diminution or disappearance of color in the

sample, when thus treated, indicates that the color is due, either partially or wholly, to iron, the sulphide of which is dissolved by dilute hydrochloric acid.

This method, of course, will not distinguish between copper and lead, but, as both metals are poisonous, this is not usually necessary, and the approximate quantity of the two metals may be estimated as above if both are present. If it is required to know which metal is present, a large quantity of the water must be evaporated to a small bulk, and a qualitative analysis made. If copper alone is found to be present, a standard solution of copper sulphate, containing 1 milligram of metallic copper in a cubic centimeter, is made up, and a colorimetric determination made, just as when the lead solution is used. A standard copper solution for this purpose is made by dissolving 3.927 grams of pure crystallized copper sulphate in distilled water, and making the solution up to 1 liter.

It is sometimes desirable to know the action of a certain water on lead pipe. To learn this, place a piece of bright lead in one vessel, and a piece of dull lead in another; cover them with the water, allow them to stand 24 hours, and then examine each sample for lead as directed above.

118. Iron.—Wanklyn states that good drinking water should not contain more than 3 parts of iron per million. This limit may be rather severe, but it is undoubtedly true that a good drinking water should not contain a large amount of iron. Water to be used in washing white goods, or in dyeing, should also contain but little of this element. To determine iron, acidify a suitable volume (200 to 500 cubic centimeters, according to indications) of the water with aqua regia, evaporate this solution to 100 cubic centimeters, pour it into a Nessler cylinder, and add 2 cubic centimeters of ammonium-sulphocyanide solution. Compare the color thus produced with the colors of standards made by adding measured quantities of standard iron solution to Nessler cylinders, diluting to 100 cubic centimeters with distilled water, and adding 2 cubic centimeters of ammonium sulphocyanide.

To make the standard solution of iron, weigh .1 gram of pure iron into a small beaker, and dissolve it in a little hydrochloric acid; add a few drops of nitric acid, and heat to boiling. Wash this solution into a liter flask, and dilute it to the mark with distilled water that is known to be free from iron. Each cubic centimeter of this solution contains .1 milligram of iron.

119. Zinc and Chromium.—These metals are best determined by evaporating a large quantity of the water to a small bulk, and applying the usual gravimetric methods. The quantitative estimation should be preceded by a qualitative examination of a concentrated sample, and the exact method of procedure made to depend on what is thus learned. In any case, acidulate a large quantity of the water with hydrochloric acid, evaporate to dryness, and heat in an air bath at 120° to 130° until the odor of hydrochloric acid is no longer perceptible. Moisten the residue thoroughly with concentrate hydrochloric acid, and add an appropriate quantity of water, the amount depending on the size of the residue. Heat this solution to boiling, filter off the silica, and wash it thoroughly with hot water. If first or second group metals are present, they must be precipitated by hydrogen sulphide, and the filtrate must be boiled to expel the last trace of this reagent. If the qualitative test has indicated that only chromium and zinc are now present, heat the water to boiling, and slowly add a slight excess of dilute ammonia while stirring continuously. Filter off the precipitated chromium hydrate, and proceed with the determination of chromium as directed in Art. **48**, *Quantitative Analysis*, Part 1.

Concentrate the filtrate from the chromium hydrate to a convenient volume, render it distinctly alkaline with sodium carbonate, and then add sufficient acetic acid to render it slightly but distinctly acid, and dissolve any precipitate formed by the carbonate. Heat the solution to incipient boiling, and precipitate the zinc as sulphide by leading a rather rapid current of hydrogen sulphide through the

solution. The zinc may be weighed as sulphide, or the precipitate may be dissolved, and the zinc determined in the solution by one of the methods given in Art. **50** *et seq.*, *Quantitative Analysis*, Part 1.

120. Arsenic.—Arsenic occurs in some waters, and, when present, it should not be overlooked. A qualitative determination is all that is ordinarily required, and for this purpose the Marsh test is generally employed. The details of this process are given in Art. **72**, *Qualitative Analysis*, Part 2. When pure zinc is employed in making this determination, the action is very slow at first, and the process becomes quite tedious. Zinc, alloyed with platinum for this purpose, is now on the market, and it appears to be a decided improvement.

If a quantitative determination is required, a large quantity of the water should be evaporated to the proper volume, and the arsenic determined in this by one of the methods given in Art. **56** *et seq.*, *Quantitative Analysis*, Part 1.

HARDNESS.

121. The determination of hardness has more to do with the scale-forming constituents of a water than with those that have an influence on its character as a drinking water, and, consequently, is probably of greater value in the examination of water for a boiler supply than in the analysis of potable waters. But if the water is for domestic use, a knowledge of how it will act in cooking utensils is of value, and this determination is of considerable importance in examining a water that is to be used for laundry purposes. It is a well known fact that when soap is added to a water containing salts of calcium or magnesium, a considerable portion of the soap is used up in precipitating these metals before any of it is available for detergent purposes. Waters containing these salts are spoken of as hard waters. They are not adapted for laundry use on account of the increased amount of soap required, and the precipitate formed in the water is

undesirable. As we have seen, hardness is divided into permanent and temporary hardness. Temporary hardness is due to salts that are precipitated by boiling the water, and permanent hardness is due to those that remain in solution after the water is boiled. As a rule, the total hardness is all that is required.

Dr. Clark devised a method for the estimation of the hardness of a water by means of a standard soap solution. The soap solution is added to the water until a permanent lather forms, and the hardness is thus learned. This method is in some respects unscientific, but it is nevertheless valuable in many instances. The results were formerly stated in degrees of hardness, and this would be the best method of reporting results if so much confusion had not entered through the use of different quantities of sample; but as degrees based on different quantities are used, such a report is without meaning unless accompanied by an explanation. To avoid confusion, we prefer to state results in parts per million of calcium carbonate or its equivalent.

122. Standardizing the Soap Solution. — Scrape 10 grams of shavings from a new cake of pure Castile soap, dissolve them in 1 liter of dilute alcohol (2 parts of absolute alcohol to 1 part of water), filter off insoluble matter, if any is present, and keep the solution in a glass-stoppered bottle. To ascertain the strength of this solution, weigh out exactly 1 gram of pure calcium carbonate, and dissolve it in the least necessary quantity of dilute hydrochloric acid. Cautiously add dilute ammonia in sufficient quantity to just neutralize the excess of acid, and dilute the solution to 1 liter. Each cubic centimeter of this solution will contain a quantity of calcium salt equivalent to 1 milligram of calcium carbonate.

Measure 10 cubic centimeters of this standard calcium solution into a glass-stoppered bottle having a capacity of about 250 cubic centimeters, and add 90 cubic centimeters of distilled water. Then add soap solution, .5 cubic centimeter at a time, and shake after each addition, until a lather

is formed that persists for 5 minutes. Note the quantity of soap solution used, and then repeat the experiment, adding .5 cubic centimeter of solution at a time at first, but only .1 or .2 at a time towards the end of the reaction. The exact amount required is thus learned. Now cleanse the bottle, introduce 100 cubic centimeters of pure distilled water, and titrate this with the soap solution in the same way, to learn the amount of soap solution used up by 100 cubic centimeters of pure water. Subtract this amount from the amount used in titrating the standard, to learn the amount used in precipitating the calcium. From this, calculate the value of 1 cubic centimeter of the soap solution in terms of calcium carbonate, and record the factor thus found on the bottle, together with the date of standardization.

An example may render this more clear. Let us suppose that 10 cubic centimeters of the soap solution are used up by the standard, consisting of 10 cubic centimeters of calcium solution and 90 cubic centimeters of distilled water, and that .8 cubic centimeter is used up by 100 cubic centimeters of distilled water. Then, 9.2 cubic centimeters of the soap solution are required for 10 milligrams of calcium carbonate, and the value of 1 cubic centimeter of soap solution in milligrams of calcium carbonate is 1.087. The soap solution should be restandardized at frequent intervals, for it is not permanent, and deteriorates quite rapidly, especially in cold weather.

123. Determination of Hardness.—Measure 100 cubic centimeters of the water into a glass-stoppered bottle of about 250 cubic centimeters capacity, and add soap solution, .5 cubic centimeter at a time, shaking after each addition, until a lather that persists for 5 minutes is formed. When a permanent lather appears to be formed, place the bottle on its side, and allow it to remain in this position for 5 minutes, or until the lather disappears. If the lather disappears in less than 5 minutes, add a little more soap, shake, and again place the bottle on its side. When the lather persists for

5 minutes, the reaction is complete. Now, from the amount of soap solution used, deduct the amount required to produce a permanent lather with 100 cubic centimeters of distilled water, multiply this quantity by the value of 1 cubic centimeter of the soap solution, and multiply the result thus obtained by 10. The total hardness of the water, expressed in parts of calcium carbonate or its equivalent per million, is thus obtained.

In order to obtain the most concordant results, the soap solution should be standardized, and all determinations made at the same temperature, preferably at 15°. It should be remembered that the method is not strictly accurate at best, and, to obtain concordant results, the same method of procedure should be adopted in every case. This is important in adding the soap solution. Not more than .5 cubic centimeter of this should be added at a time, even though the approximate amount required is known. If a water is so hard that 100 cubic centimeters of it require more than 20 cubic centimeters of the soap solution, a second determination should be made, using 50 cubic centimeters of the sample and 50 cubic centimeters of distilled water. Better results are obtained in this way, for the large precipitate formed in the undiluted sample appears to interfere with proper lathering.

It is usually sufficient to determine the total hardness, but, in some cases, the temporary and the permanent hardness are required. When this is the case, determine the total hardness; then boil 100 cubic centimeters of the water, filter off any precipitate formed, add distilled water to make up for the portion evaporated, and determine the permanent hardness in this sample. The difference between the total hardness and the permament hardness is the temporary hardness.

INTERPRETATION OF RESULTS.

124. In no branch of chemical work, is the exercise of judgment more necessary than in forming an opinion as to the quality of potable water from the results obtained by

analysis. The chemist should make himself as familiar as possible with the history of the water, and then should consider all the results together in the light of all that is known of the water, and in regard to their bearing on each other. In the case of very good or very bad waters, it is a comparatively easy matter to decide as to their quality; but, with many samples lying between these two extremes, the most careful study is required. The following figures, taken from the standards of purity of drinking water specified by the Michigan State Laboratory of Hygiene, may be of value to the student:

1. The total solids should not exceed 500 parts per million.

2. The chlorine should not exceed 12.1 parts per million.

3. The free ammonia should not exceed .05 part per million.

4. The albuminoid ammonia should not exceed .15 part per million.

5. The oxygen consumed by organic matter should not exceed 2.2 parts per million.

6. The nitrogen as nitrate should not exceed .9 part per million.

7. The best water contains no nitrous acid, and any water that contains nitrites in quantity sufficient to be estimated should not be regarded as a safe drinking water.

These dogmatic statements should not be accepted as final, and indeed no fixed limits can be prescribed, but, as we have pointed out, the results must be considered in their relation to one another, and in the light of what is known of the water. For example, a water contaminated by sewage, and found to contain 12.1 parts per million of chlorine, and .15 part per million of albuminoid ammonia, should be condemned absolutely; while the water of a pond or stream in a heavily wooded district containing salt deposits, might contain these quantities of the constituents mentioned, and still be fairly wholesome.

EXAMINATION OF ICE.

125. Chemists are frequently called on to examine samples of ice. In such cases, the ice is allowed to melt, and the water thus obtained is examined in the usual manner. It should not be allowed to melt exposed to the air, however, but should be enclosed in a jar with a tight-fitting glass stopper. A 2-gallon jar with a wide mouth serves well for the purpose. Wash the jar well with distilled water, and introduce the ice in as large pieces as possible, taking care not to touch the ice with the hands more than is necessary. Small fire tongs, thoroughly cleaned, serve well in handling the ice. Insert the stopper, and allow about one-fifth of the ice to melt at the temperature of the room. Pour off the water, thus thoroughly washing the remaining ice, insert the stopper again, and allow the rest of the ice to melt. Using the water thus obtained as a sample, make the ordinary determinations in the usual manner.

Free ammonia may be present in ice in about the same quantity as in the water from which it is obtained, but, for the other constituents, the limits of purity are lower. Cairns states that the albuminoid ammonia should be less than .05 part per million. This seems rather severe, but the albuminoid ammonia in most samples of ice examined by the writer has fallen within this limit.

WATER FOR BOILER SUPPLY.

126. Little is cared about the sanitary quality of a water to be used as a boiler supply, but the mineral or scale-forming constituents of the water are important in this case. The principal scale-forming constituents are the carbonates of calcium and magnesium, and calcium sulphate; but, in order to learn the quantities of these constituents present, it is necessary to determine other constituents not generally considered as scale-forming. Sometimes the determination of two or three constituents is all that is required, but such an examination would prove of little service in many cases. A method that will give the most complete idea of the water

obtainable by the ordinary methods of analysis, is as follows: First determine the total solids as directed in Art. **85**, as this will serve as a guide in later work, and then proceed with the analysis of the mineral residue. While carrying on this analysis, determine the chlorine and the hardness as directed in Arts. **87** and **123**, respectively.

127. Determination of Silica.—Measure out an appropriate quantity of the water (from 1 to 10 liters, depending on the amount of solids found), acidify it with hydrochloric acid, and evaporate to dryness in a platinum dish. The evaporation may be carried on over a Bunsen burner, adding successive portions of the water until the sample is all in the dish, and reduced to rather small bulk, but should be completed over a water bath. When dry, remove the dish from the water bath to an air bath, and heat it at 120° to 130° until the odor of hydrochloric acid is no longer perceptible. Moisten the residue thoroughly with concentrate hydrochloric acid, add from 25 to 50 cubic centimeters of water, and boil to dissolve the soluble salts. Filter, wash thoroughly with hot water, ignite in a platinum crucible, and weigh.

If the residue is very small, it is almost certain to be composed entirely of silica, and an examination is scarcely necessary; but if it is of any considerable size, it may contain calcium sulphate, and should be treated as follows: Fuse the residue with sodium carbonate, dissolve the fusion in water and hydrochloric acid, evaporate to dryness, and heat at 120° to 130° to render the silica insoluble. Moisten the residue with hydrochloric acid, add 25 to 50 cubic centimeters of water, and boil to dissolve soluble salts. Filter off the insoluble residue, wash thoroughly with hot water, ignite, and weigh as silica SiO_2.

Heat the filtrate from the silica to boiling, add ammonia to render it alkaline, and then ammonium oxalate to precipitate the calcium; allow it to stand for at least 3 hours, filter, wash, ignite, and weigh as calcium oxide. Calculate this to calcium sulphate, for this portion of the calcium, at least, occurs as sulphate in the water.

128. Determination of Iron Oxide and Alumina.—Heat the filtrate from the first insoluble residue to boiling, and cautiously add a very slight excess of ammonia. If a copious light-colored precipitate separates, it may contain calcium. In this case, add a little more ammonia, and then dissolve the precipitate in a slight excess of hydrochloric acid. Enough ammonium chloride will thus be formed in the solution to prevent the precipitation of calcium. Now render the solution faintly alkaline with ammonia, continue the boiling for a few moments, allow the precipitate to settle, and filter off the hydrates of iron and aluminum. Wash the precipitate with hot water, ignite in a platinum crucible, and weigh as the oxides of iron and aluminum $Fe_2O_3 + Al_2O_3$. It is unnecessary to separate the oxides in this case, and they should be reported as they are weighed.

129. Determination of Calcium.—At this point, the filtrate will usually be rather large, and should be evaporated to a suitable volume. Then, to the gently boiling liquid, add a few cubic centimeters of ammonia and a moderate excess of ammonium oxalate, continue to boil for a few minutes, and allow the precipitate to settle. Filter, wash thoroughly with hot water containing a few drops of ammonia, ignite intensely over the blast lamp, and weigh as calcium oxide.

130. Determination of Magnesium.—Evaporate the filtrate from the calcium oxalate to a rather small bulk, add a moderate excess of sodium-ammonium phosphate solution while stirring vigorously, add about one-fourth the volume of the liquid of strong ammonia, and cool the solution by standing it in ice water. If a precipitate begins to form at once, when the microcosmic salt or the ammonia is added, the reagent should be introduced, a drop at a time, and the solution stirred after the addition of each drop. Allow the solution to stand 6 hours in a cool place for the precipitate to settle. Filter, wash with one-third-strength ammonia, ignite intensely, and weigh as magnesium pyrophosphate $Mg_2P_2O_7$. Calculate the magnesium to oxide MgO.

131. Determination of Sulphuric Acid.—Acidulate from 1 to 5 liters of the water with hydrochloric acid, evaporate to a small bulk over a burner, and then to dryness on a water bath. Moisten the residue with hydrochloric acid, dissolve it in water, filter off any silica that remains, and wash it thoroughly with hot water. The filtrate should amount to about 100 cubic centimeters. Heat it to boiling, add a moderate excess of barium chloride, and continue the boiling for a few moments. Allow the precipitate to settle, filter, wash with hot water, ignite moderately, and weigh as barium sulphate. From this, calculate the amount of sulphur trioxide in a liter. If a filter paper is used in filtering, the precipitate should be dried and removed from the paper before ignition, to avoid reduction of the precipitate by the burning paper, and a good quality of paper must be used to avoid danger of the precipitate running through. A Gooch crucible is preferred for this purpose by many chemists.

132. Determination of Alkalies.—Acidulate from 1 to 5 liters of the water with a few drops of hydrochloric acid, and evapórate to about 75 cubic centimeters; then add a saturated solution of barium hydrate as long as it produces a precipitate. Heat to boiling, filter, and wash the precipitate until a test of the washings, acidified with nitric acid, fails to give a reaction for hydrochloric acid on the addition of silver nitrate. Evaporate the filtrate to about 75 cubic centimeters, remove from the burner, add a few drops of ammonia, then a strong solution of pure ammonium carbonate as long as a precipitate forms, and allow the solution to stand for some time, stirring occasionally until the precipitate becomes granular. Filter and wash the precipitate with water containing a very little ammonium carbonate and a few drops of ammonia. After adding a few drops of hydrochloric acid, evaporate the filtrate and washings to dryness in a platinum dish over a water bath, place the dish in an air bath heated to about 100°, and gradually increase the temperature to 130° or 140°. Then cautiously heat the

dish to dull redness over a burner to expel ammonium salts, but take care not to heat it sufficiently to volatilize potassium chloride. Dissolve the residue in about 10 cubic centimeters of water, by the aid of very gentle heat, add a few drops of barium hydrate, then a few drops of ammonia, and a slight excess of ammonium carbonate, and allow the solution to stand a short time, stirring occasionally. Filter and wash the precipitate with water containing a very little ammonium carbonate and a drop or two of ammonia. After adding a few drops of hydrochloric acid, evaporate the filtrate to dryness in a weighed platinum dish over a water bath; place the dish in an air bath heated to about 100°, and increase the temperature to about 140°; then heat it very cautiously over a burner to expel all ammonium salts, cool in a desiccator, and weigh as soon as cool. The residue in the dish now consists of the chlorides of sodium and potassium.

Dissolve the residue of mixed chlorides in the least necessary quantity of water, add a solution of platinum chloride that is as nearly neutral as possible, in excess of the quantity required to unite with all the potassium and sodium present, and evaporate to a pasty consistency on a water bath in which the water is maintained at just about the boiling point, but is not allowed to boil vigorously. Allow the mass to cool, add 35 cubic centimeters of 80-per-cent. alcohol and let it stand in a moderately warm place for an hour, stirring from time to time. If the precipitate is rather large, filter on a paper that has been dried at 120° or in a Gooch crucible, wash thoroughly, but not excessively, with 80-per-cent. alcohol, dry at 120°, and weigh as potassium-platinum chloride K_2PtCl_6. If the precipitate is very small, it is best, after filtering and washing, to dissolve it with a little water; allow the solution to run into a weighed platinum dish, evaporate to dryness on a water bath, heat at 125° in an air bath, cool, and weigh as K_2PtCl_6. Calculate the potassium to chloride, subtract this from the weight of mixed chlorides previously obtained, to get the weight of sodium chloride, and calculate the potassium and sodium to oxides K_2O and Na_2O.

133. Grouping the Constituents.—The most rational method of reporting the results of a mineral analysis of a water would be to report just what is found, without attempting to show how the constituents were combined in the water. This method, however, would only show what scale-forming constituents are present to a person acquainted with chemical combination; and to make the analysis as useful as possible, an attempt is usually made to report the compounds as they exist in the water. Careful experiments have shown that if the constituents are grouped according to the following rule, the report will show what compounds exist in waters ordinarily used as potable water or for boiler supply.

Combine the chlorine with the sodium, and if there is more than is required to saturate this, combine it next with potassium; if there is chlorine still left, combine it next with magnesium, and, finally, with calcium. Combine the sulphuric acid with potassium first, if there is any left, and the sodium is not saturated with chlorine; combine the remaining sulphuric acid with the remaining sodium, then with calcium, and, finally, with magnesium. Any of these metals now remaining uncombined are calculated to carbonates. This method of grouping the constituents very nearly represents the facts so far as they can be ascertained for most waters used in boilers and for domestic purposes. There are exceptions to this rule, however, notably in the case of artesian wells, and, especially, mineral waters.

QUANTITATIVE ANALYSIS.

(PART 4.)

GAS ANALYSIS.

GENERAL PRINCIPLES.

1. Although the principles underlying the various forms of gas analysis are themselves of a simple nature, the apparatus employed and the manipulative details involved are in some cases of a comparatively complicated and intricate nature. This is especially the case when the analysis is to be executed with that high degree of exactness essential to scientific research, and, until quite recently, these very exact but also very slow methods of gas analysis were also the only available ones for practical purposes. The growing demand of late years for simpler and more rapid methods, sufficiently accurate for technical purposes, has originated simpler and more rapid methods, and has led to the invention of various forms of gas apparatus, which not only yield good results, but also demand only a minimum amount of time, energy, and operative skill.

It is not within the scope of this Course to dwell upon the more complicated and delicate methods of gas analysis used in research work, but it is our aim to make the student familiar with the simpler and practical determinations he is most likely to be called on to perform.

2. Determination of Gases.—The methods by which gases are determined may be classified according to the following: (1) Absorption of the gas in a suitable reagent and subsequent titration; (2) absorption of the gas in a suitable reagent and subsequent measurement of the residual gas; (3) combustion of the gas, with the subsequent measurement of the contraction and estimation of the carbon dioxide, if any is formed.

A few examples will serve to give the student a general idea of the principles of each of the above enumerated methods.

1. *By Absorption in a Suitable Reagent and Subsequent Titration.*—The carbon dioxide present in a gaseous mixture, as, for instance, air, may be determined by bringing a known volume of the gas into contact with an excess of a standard solution of barium hydrate. Barium carbonate is thereby precipitated, and the excess of barium hydrate is determined by titration with a standard solution of oxalic acid.

2. *By Absorbing the Gas in a Suitable Reagent and Subsequent Measurement of the Residual Gas.*—The carbon dioxide in a mixture of gases is determined by exposing a measured volume of the mixture to the action of caustic potash, and, after the whole of the carbon dioxide has been absorbed, the volume of the residual gas is measured. The difference, or the *contraction*, represents the carbon dioxide that was present.

3. *By Combustion of the Gas, with the Subsequent Measurement of the Contraction and Estimation of the Carbon Dioxide, if any is Formed.*—Hydrogen in a gaseous mixture may be estimated by adding to a known volume of the mixture a measured volume of oxygen or air more than sufficient to combine with all the hydrogen. These are caused to unite (by methods to be described later), and the contraction ascertained by again measuring the gas. Since 2 volumes of hydrogen and 1 volume of oxygen unite to form water (which practically occupies no volume), two-thirds of the contraction represents the hydrogen originally present. When the gas to be estimated contains carbon and hydrogen (as in

marsh gas, ethylene, etc.), after the contraction due to combustion has been measured, the volume of carbon dioxide produced is determined by absorption with caustic potash and measurement of the residue.

ESTIMATION OF GASES BY ABSORPTION AND SUBSEQUENT TITRATION.

ESTIMATION OF CARBON DIOXIDE IN AIR.

3. The most varied experience has shown that, through the process of breathing, the air acquires properties that cause it to act deleteriously on health when the products of breathing exceed a certain limit. Since we are not able, by ordinary means, to determine the other substances that are here formed, we make use of von Pettenkofer's suggestion and judge of the purity of the air by the percentage of carbon dioxide present. According to von Pettenkofer, the carbon dioxide in the air should not be raised, by breathing, to over .1 per cent.

The process best suited to the quantitative determination is that first used by Saussure and modified by von Pettenkofer, and generally known as **von Pettenkofer's methods.** The sample of air to be examined is contained in a large, wide-mouthed glass jar, the exact capacity of which is known, and that can be closed with an air-tight fitting rubber stopper. The temperature of the air and the atmospheric pressure are noted at the time the sample is taken. A measured volume of a solution of barium hydrate of known strength is introduced into the jar, and thoroughly shaken up with the enclosed air until the carbon dioxide is all absorbed. Aliquot portions of the liquid are then withdrawn, and titrated with a solution of oxalic acid of known strength.

4. Standard Oxalic Acid.—In order to simplify the subsequent calculations, the strength of the oxalic-acid solution

may be made up so that 1 cubic centimeter is equivalent to 1 cubic centimeter carbon dioxide measured under standard conditions, that is to say, 1 cubic centimeter of the acid is capable of saturating a quantity of barium hydrate that would be decomposed by this volume of carbon dioxide, the weight of which is .00197 gram. Oxalic acid of this strength would contain 5.6442 grams of the crystallized acid $H_2C_2O_4,2H_2O$ in 1 liter; but, as dilute solutions of oxalic acid are not stable, it is advisable to prepare a solution that contains 56.442 grams of $H_2C_2O_4,2H_2O$ per liter, and to withdraw an aliquot proportion and dilute it whenever required. Thus, 56.442 grams of dry, crystallized oxalic acid are exactly weighed out, dissolved in cold, air-free water (that is, distilled water that has been recently boiled to expel all carbon dioxide, and quickly cooled), and the solution made up to 1 liter. For use, 10 cubic centimeters are transferred to a 100-cubic-centimeter flask by means of a pipette, and the solution diluted to 100 cubic centimeters with air-free water.

5. Barium-Hydrate Solution.—Place 40 to 50 grams of crystallized barium hydrate $Ba(OH)_2,8H_2O$, powdered or crushed, in a large glass-stoppered bottle, and add 1 liter of water. The mixture is thoroughly shaken from time to time, until the water is saturated, after which it is allowed to settle. The clear liquid is carefully decanted or filtered into another glass-stoppered bottle, and diluted with an equal volume of water. This solution will possess approximately the same relative strength as that of the oxalic acid previously mentioned. A solution of exact equivalent strength, of which 1 cubic centimeter = .00917 gram CO_2 (i. e., 1 cubic centimeter CO_2 at normal temperature and pressure), would contain 14.11 grams of $Ba(OH)_2,8H_2O$ per liter. Such a solution cannot be obtained by direct weighing, as, the salt being efflorescent, its state of hydration is uncertain; and it also absorbs atmospheric carbon dioxide. A saturated solution at the ordinary temperature contains about 32 grams per liter; hence, if this be diluted with its

own volume of water, the solution, as first prepared, will contain about 16 grams per liter. As the solution constantly undergoes change by the absorption of atmospheric carbon dioxide, its value must be determined every time before it is used by titration against the standard oxalic acid. The stopper of the bottle containing the barium-hydrate solution should be greased, so as to exclude the air as much as possible.

6. Standardizing the Barium-Hydrate Solution.—In a small flask are placed 20 cubic centimeters of standard oxalic acid and then 25 cubic centimeters of the barium-hydrate solution added. The solution is then neutralized by slowly running in more oxalic acid by means of a burette until the liquid ceases to give any indication of a brown color when a drop of it is placed on a piece of turmeric paper. The alkali is gradually neutralized by the oxalic acid; the brown color, which at first is very evident, gradually shows more and more as a faint fringe of color round the edge of the moistened spot on the turmeric paper, until finally it disappears. Suppose, for instance, that 28 cubic centimeters of the oxalic acid are used; then, 100 cubic centimeters of this barium-hydrate solution would require 112 cubic centimeters of the oxalic acid to exactly neutralize it.

7. Determination of Carbon Dioxide.—A large glass jar, whose mouth is sufficiently wide to admit the hand, so that it may be conveniently wiped dry inside with a cloth, is fitted with a rubber stopper. A hole is bored in the stopper, and this hole is closed with a piece of glass rod. The capacity of the jar is ascertained by filling it with water up to the stopper, and measuring the volume of the water. As it is evident that when the amount of carbon dioxide present is small, the accuracy of the determination is increased by using larger volumes of air; it is advisable that the jar should hold from 8 to 10 liters, if possible, but not less than 5 liters. Its exact capacity should be scratched on the vessel.

The jar is filled with the air to be tested by leading into it, right to the bottom of the jar, a piece of rubber tubing attached to a pair of bellows and blowing a stream of air for about 5 to 6 minutes, in order to insure complete displacement of the air already in the vessel. The stopper is then inserted. The temperature of the air in the immediate vicinity of the jar is noted, and also the height of the barometer at the same time. By means of a pipette, 100 cubic centimeters of the barium-hydrate solution are then delivered in the jar through the hole in the stopper, and the glass rod is immediately replaced. The liquid is then made to wet the surface of the glass by slowly revolving the vessel upon its side; and it is left in contact with the gas, being shaken at intervals for about 30 to 40 minutes, by which time all the carbon dioxide will have been absorbed. When the absorption of the carbon dioxide is complete, 25 cubic centimeters of the turbid liquid are withdrawn by means of a pipette, to which a piece of glass tubing has been attached in order that the bottom of the jar may be reached. This arrangement is introduced through the hole in the rubber stopper, as shown in Fig. 1. When the pipette is full, the piece of rubber is detached, and the liquid allowed to drip from the pipette until it reaches the graduation mark. The measured volume is then transferred to a beaker, and immediately titrated with oxalic acid, exposure to the air being avoided as much as possible. The end of the reaction is indicated by means of turmeric paper, used as described in Art. **6.** A duplicate titration should be made with a second portion of the liquid. Some chemists prefer to use a solution of phenol phthalein in alcohol as an indicator. In this case, about 2 cubic centimeters of this indicator are added to the liquid, and the

FIG. 1.

oxalic acid added until the liquid becomes neutral, which is indicated by the disappearance of the color.

Since 25 cubic centimeters (out of the 100 cubic centimeters of the barium-hydrate solution originally placed in the jar) have been used for titration, the volume of oxalic acid used, multiplied by 4, will give the amount of oxalic acid required to neutralize the 100 cubic centimeters of the barium-hydrate solution after the absorption of the carbon dioxide in the known volume of air. This, obviously, will be less than that required by 100 cubic centimeters of the original barium-hydrate solution by just the volume of carbon dioxide that was contained in the sample of the air.

The following details of an analysis will make this determination perfectly understood:

Capacity of glass jar = 10.5 liters.
Temperature of the air = 17°.
Barometer reading = 769 mm.

Then, $$\frac{10.5 \times 273 \times 769}{(273+17) \times 760} = 10.001 \text{ liters},$$

which is equal to the volume of the sample at normal temperature and pressure.

The value of the barium-hydrate solution is 100 c. c. = 112 c. c. of the standard oxalic-acid solution; 100 c. c. of the barium hydrate were used for absorption; 25 c. c. were taken out for titration; 25 c. c. required 27.10 c. c. of standard oxalic acid; therefore, 100 c. c. would require $27.10 \times 4 = 108.4$ c. c. oxalic acid. $112 - 108.4 = 3.6$ c. c. = the volume of oxalic acid, which is equivalent to the carbon dioxide absorbed by the 100 c. c. of barium-hydrate solution.

But, since 1 c. c. of oxalic acid = 1 c. c. CO_2 at normal temperature and pressure, 3.6 c. c. oxalic acid = 3.6 c. c. CO_2 present in 10.001 liters or 10,001 c. c. of air.

Therefore, $$\frac{3.6 \times 100}{10{,}001} = .0359 = \text{percentage of } CO_2 \text{ by volume.}$$

8. Since the presence of barium carbonate does not interfere with the titration, some chemists prefer to titrate

directly in the same vessel in which the air has been collected. This method has the advantage that the barium-hydrate solution is the least exposed to air. For this purpose, a liter flask is employed, which is fitted with a rubber stopper having two perforations that are closed with pieces of glass rod. After sampling the air and adding 10 cubic centimeters of barium-hydrate solution, the burette containing the standard oxalic acid is inserted into one of the perforations, as shown in Fig. 2, and the titration carried out as previously described. As an indicator, about 1 cubic centimeter of phenol phthalein in alcohol is used. The titration is finished as soon as the last trace of color disappears. If the increased pressure resulting inside the flask checks the flow of the liquid from the burette, this pressure is removed by lifting the glass stopper closing the second perforation. The only disadvantage of this method is that but a comparatively small volume of air can be used.

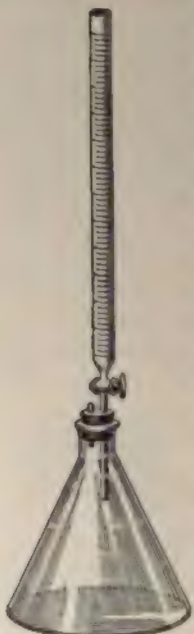


FIG. 2.

ESTIMATION OF SULPHUR DIOXIDE IN FURNACE GASES.

9. By means of a pipe inserted into the flue, a measured volume of the furnace gases is aspirated, with a suitable aspirator, through a known volume of a dilute standard solution of iodine, and the excess of iodine titrated with a standard solution of sodium thiosulphate.

10. Standard Iodine Solution.—Pure resublimed iodine to the amount of 12.7 grams, is powdered and weighed out into a liter flask. About 20 grams of potassium iodide (free from iodate), dissolved in 200 cubic centimeters of water, are added, and the mixture gently shaken until the

iodine is entirely dissolved. The solution is then diluted up to the liter with water at 15° and preserved in a well-fitting stoppered bottle in the dark; 1 cubic centimeter of this solution will contain .0127 gram of iodine, and is equivalent to .0032 gram of SO_2. It is, however, more convenient in this case and simplifies the calculation, to employ solutions of such strength that 1 cubic centimeter shall equal 1 cubic centimeter SO_2 measured at normal temperature and pressure, i. e., .002867 gram SO_2 instead of .0032. Such a solution will contain 11.379 grams of iodine per liter, and may be most conveniently obtained by diluting 100 cubic centimeters of the above solution to 111.6 cubic centimeters. In case the percentage of SO_2 in the gas under examination is comparatively small, it is better to employ a solution of one-tenth this strength, in which 1 cubic centimeter = .1 cubic centimeter SO_2.

11. Standard Sodium-Thiosulphate Solution.—To obtain a standard solution, 1 cubic centimeter of which is equivalent to 1 cubic centimeter SO_2, i. e., .002867 gram SO_2, 22.22 grams of sodium thiosulphate $Na_2S_2O_3, 5H_2O$, which has been carefully powdered, are weighed out into a liter flask and dissolved in water. The solution is then diluted to the 1,000-cubic-centimeter mark with water at 15°. If 100 cubic centimeters of this solution are again diluted to 1,000 cubic centimeters, each cubic centimeter is equivalent to .1 cubic centimeter SO_2. As it is practically impossible to obtain sodium thiosulphate containing exactly the theoretical amount of water of crystallization, it is preferable to weigh out about 23 grams of the salt, and titrate it against the iodine solution of known strength, and from the results, calculate the amount of water that has to be added to make 1 cubic centimeter equivalent to exactly 1 cubic centimeter of the iodine solution.

12. Starch Solution.—The starch solution, serving as an indicator, is prepared by mixing 1 or 2 grams of dry starch in a medium-sized beaker with 5 or 6 cubic

centimeters of cold water. A considerable quantity of boiling water is then poured on it. As the hot water is being added, the opaque white appearance, which the mixture presents at first, changes almost suddenly to that of a semi-translucent gelatinous substance. At this point, the addition of the boiling water is stopped, and the beaker nearly filled up with cold water. It is allowed to settle, and the clear liquid poured off for use. This starch solution should be made up fresh every time, as it will not keep more than a day.

13. Determination of Sulphur Dioxide.—The apparatus used in this determination is known as **Reich's apparatus;** it consists of a double-necked absorption bottle *a*, the aspirator *b*, and the glass cylinder *c*. These are supported by a convenient stand, as shown in Fig. 3. The rubber tube joining *a* and *b* is about 30 centimeters long; 100 cubic centimeters of the $\frac{n}{100}$ iodine solution are placed in the bottle *a*, and the aspirator *b* is filled with water. Before making a determination, the air in the tubes leading to the apparatus is displaced by the gas to be examined. The apparatus is tight if, after a short time and as soon as the air in *a* is correspondingly expanded, the water ceases entirely to flow from the aspirator. In making the determination, the stop-cock *c* is opened, and the amount of water that is necessary to draw over sufficient gas to decolorize the iodine solution is measured in the cylinder *c*. During the determination, the bottle *a* is frequently shaken. The volume of water that has run out is equal to that of the gas taken, and the quantity of sulphur dioxide

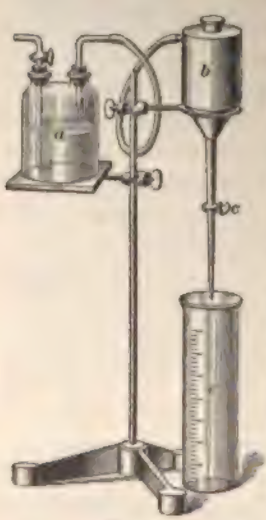


FIG. 3.

can approximately be told from the amount of iodine used. During the experiment, the temperature of the water is taken (which will be the temperature of the gas) and the height of the barometer is noted.

When 8 or 10 liters* of gas have in this way been aspirated through the iodine solution, the process is stopped, and 25 cubic centimeters of the iodine solution are transferred to a beaker and titrated with the standard sodium thiosulphate. As soon as the red-brown color of the iodine solution changes to a straw color, 1 or 2 drops of dilute starch solution are added, and the titration continued, drop by drop, until the blue color is entirely discharged. A duplicate titration is made in a second portion of the solution.

The following record of an analysis will make this determination more clear.

Gas drawn from the flue of a coke furnace:

Volume of water drawn from aspirator	= 8.25 liters.
Temperature	= 16°.
Atmospheric pressure	= 765 mm.

Volume of gas operated upon equals

$$\frac{(8.25 \times 273) \times 765}{(273 + 16) \times 760} = 7.8445 \text{ liters}$$

at normal temperature and pressure.

100 c. c. of iodine solution are employed in the absorption flask.

1 c. c. = 1 c. c. of thiosulphate = .1 c. c. SO_2 at normal temperature and pressure.

After absorption, 25 c. c. of iodine solution required 18.2 c. c. sodium thiosulphate.

* When the gas is very rich in sulphur dioxide, as, for instance, in the flue gases from the sulphur burner in vitriol works, a much smaller volume, say 1 liter, need be drawn through the apparatus, and, in the final correction of the volume of gas operated on, the volume of sulphur dioxide that has been absorbed must be deducted from the volume of water measured out of the aspirator. In the example here given, where the amount of sulphur dioxide is small, these corrections are left out, as they would not affect the third decimal figure.

Volume of thiosulphate required for 100 c. c. = 18.2×4 = 72.8 c. c., and volume of SO_2 absorbed equals

$$\frac{100-72.8}{10} = 2.72 \text{ c. c.}$$

Hence, 7,844.5 c. c. of the furnace gas contain 2.72 c. c. SO_2, or

$$\frac{2.72 \times 100}{7,844.5} = .0346 \text{ percentage } SO_2 \text{ by volume.}$$

ESTIMATION BY ABSORPTION AND MEASUREMENT OF RESIDUAL GAS.

14. The processes employed by this method differ from the foregoing, in that they involve (1) manipulation of comparatively small volumes of gas, and (2) the accurate measurement of these volumes.

For the manipulation of small volumes of gas, special apparatus is required; and for the accurate measurement of gaseous volumes, special precautions are necessary.

15. Simple Gas Burette.—The simple gas burette, which is shown in Fig. 4, consists of two glass tubes *a* and *b*, which are set in iron feet and are connected by a thin rubber tube about 120 centimeters long. To facilitate the cleaning of the burettes, the rubber tube is cut in two parts, and the two ends joined by a piece of glass tubing. Inside the feet, the tubes *a* and *b* are bent at right angles and conically drawn out. The end projecting from the iron is about 4 millimeters external diameter, and is somewhat corrugated, so that the rubber can be tightly fastened to it by winding it with thin wire. The measuring tube *b* ends at the top in a thick-walled tube *c* of from $\frac{1}{2}$ to 1 millimeter internal diameter, and about 3 centimeters long. Over this, a short piece of new, black, rubber tubing *d* is wired on. The rubber tube is closed by a Mohr pinch cock *f*, which is put on close to the end of the capillary. The graduated measuring tube *b* holds 100 cubic centimeters, the lowest mark being slightly above the iron foot. The cubic centimeters are divided into fifths, and the

graduation runs up and down. The tube *a*, generally known as the level tube, is somewhat widened at the upper end, to facilitate the pouring in of liquids.

FIG. 4.

16. Manipulation of the Gas Burette. Fill the tubes *a* and *b*, Fig. 4, with water, taking care to drive all the air out of the connecting rubber tube by either raising or lowering the tubes; then join the burette to the vessel containing the gas by means of a glass or rubber tube filled with water. This connecting tube can be easily filled with water by raising the level tube.

To fill the burette with the gas to be examined, grasp the tube *a* in the left hand, close the rubber tube by pressing it between the little finger and the palm of the hand, and pour out the water in *a*. Place the level tube on the floor and open the pinch cock *f*. The water will now flow into the level tube and the gas will be drawn into the burette. When *b* is filled with the gas, close the pinch cock *f*, disconnect *b* from the gas holder, and, after the liquid has run down

from the walls of the burette, take up the tubes by the iron feet and, by raising or lowering, bring the water in the tubes to the same level. The gas is now under atmospheric pressure and its volume is read off. To measure off exactly 100 cubic centimeters, bring somewhat more than 100 cubic centimeters of the gas into the burette, close the latter with the pinch cock, and allow the water to run down the walls of the burette. Now compress the gas to a little less than 100 cubic centimeters by raising the level tube, close the rubber tube with the thumb and first finger of the left hand, set the level tube on the table, and, raising the burette with the right hand to the level of the eye, carefully open the rubber tube and let the water run back until the meniscus stands at the 100-cubic-centimeter mark. Keeping the rubber still compressed, open the pinch cock for a moment. The excess of the gas will escape, and there remains in the burette exactly 100 cubic centimeters of gas under atmospheric pressure.

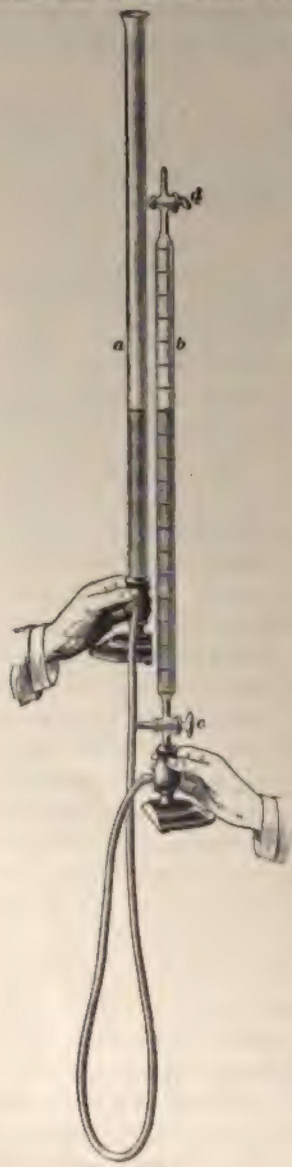


FIG. 5.

17. Modified Winkler Gas Burette.—The modified Winkler gas burette shown in Fig. 5 consists of the level tube *a* and the measuring tube *b* connected by a thin rubber tube about 120 centi-

meters long. The glass tube *b* is about 100 cubic centimeters capacity, provided with the simple glass stop-cock *d*, and the three-way stop-cock *c*, which allows of communication being established with the level tube or with the outer air at will. This will be seen more clearly in Fig. 6. The space between the two stop-cocks is divided into exactly 100 equal parts, with subdivisions of one-fifth cubic centimeter each, and the graduations are numbered in both directions. The thick-walled tube (Fig. 5) must have a diameter of from only ½ to 1 millimeter, so that bubbles of the gases that are passed in and out cannot stop in this tube. The manipulation of the burette is practically the same as that described in the preceding article.

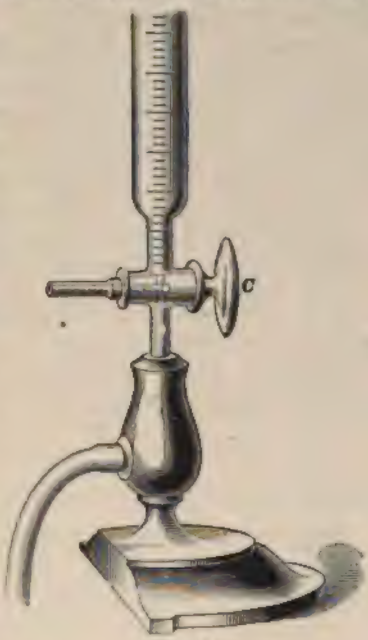


FIG. 6.

18. Correction of Gaseous Volume.—The volume of gas has been briefly treated in sections on *Physics* and *Theoretical Chemistry*, but a short repetition and expansion of the subject appears appropriate here. It has been stated in the sections mentioned, that the volume of a given weight of a gas depends on the pressure and the temperature; in gas analysis, however, a third factor has to be taken into account, namely, the degree of humidity of the gas at the time the measurement is made.

In order, therefore, that the various volumes observed during an analysis shall be comparable with one another, it is necessary either that the conditions mentioned should remain constant throughout, or that the volumes measured

under different conditions should be reduced by calculation to one common standard.

In exact methods of analysis, the latter plan is invariably adopted, but in the more rapid and somewhat rougher methods employed for technical purposes, the analysis may usually be carried out without disturbing the uniformity of conditions to an extent that will introduce any material error in the results. The recognized standard to which gaseous volumes are reduced is the volume that the gas would occupy at 0° and under a pressure of 760 millimeters, *when in the dry state.*

19. Correction of Temperature.—The coefficient of expansion is usually taken as $\frac{1}{273}$, or .003665 (see Art. **89**, *Theoretical Chemistry*); therefore, the volume at 0° equals the volume at $t°$ divided by $1 + .003665\,t$. Hence,

$$V_0 = \frac{V}{1 + .003665\,t} \text{ or } \frac{V \times 273}{273 + t} \qquad (1.)$$

where V_0 = volume at 0°, and V = volume at $t°$.

20. Correction of Pressure.—According to Mariotte's law, quoted in Art. **88**, *Theoretical Chemistry*, the volume of a gas being inversely as the pressure,

$$V_0 = \frac{V\,P}{760}, \qquad (2.)$$

where V = volume at P pressure; or, making the corrections for temperature and pressure together, we obtain the formula

$$V_0 = \frac{V\,P}{760(1 + .003665\,t)}, \text{ or } \frac{V\,P \times 273}{760 \times (273 + t)}. \qquad (3.)$$

21. Correction for Tension of Aqueous Vapor.—The aqueous vapor present in a gas exerts a pressure in opposition to the barometric pressure; hence, the volume of gas is increased by the presence of aqueous vapor. If the gas is saturated with aqueous vapor, and an excess of water, however indefinitely small, is present, then the pressure or tension of the aqueous vapor is independent of change of pressure, varying only with change of temperature. The *tension of aqueous vapor* has been experimentally determined for every degree of temperature, and in Table 1 will be found the tension or pressure, in millimeters of mercury, of the vapor of water between the temperatures 5° and 25°.

TABLE 1.

TENSION OF AQUEOUS VAPOR IN MILLIMETERS OF MERCURY FOR EACH FIFTH OF A DEGREE FROM 5° TO 25°.

C°.	t mm.	C°.	t mm.	C°.	t mm.	C°.	t mm.
5.0	6.5	10.0	9.2	15.0	12.7	20.0	17.4
.2	6.6	.2	9.3	.2	12.9	.2	17.6
.4	6.7	.4	9.4	.4	13.0	.4	17.8
.6	6.8	.6	9.5	.6	13.2	.6	18.0
.8	6.9	.8	9.7	.8	13.4	.8	18.3
6.0	7.0	11.0	9.8	16.0	13.5	21.0	18.5
.2	7.1	.2	9.9	.2	13.7	.2	18.7
.4	7.2	.4	10.1	.4	13.9	.4	19.0
.6	7.3	.6	10.2	.6	14.1	.6	19.2
.8	7.4	.8	10.3	.8	14.2	.8	19.4
7.0	7.5	12.0	10.5	17.0	14.4	22.0	19.7
.2	7.6	.2	10.6	.2	14.6	.2	19.9
.4	7.7	.4	10.7	.4	14.8	.4	20.1
.6	7.8	.6	10.9	.6	15.0	.6	20.4
.8	7.9	.8	11.0	.8	15.2	.8	20.6
8.0	8.0	13.0	11.2	18.0	15.4	23.0	20.9
.2	8.1	.2	11.3	.2	15.6	.2	21.1
.4	8.2	.4	11.5	.4	15.7	.4	21.4
.6	8.3	.6	11.6	.6	15.9	.6	21.7
.8	8.5	.8	11.8	.8	16.1	.8	21.9
9.0	8.6	14.0	11.9	19.0	16.3	24.0	22.2
.2	8.7	.2	12.1	.2	16.6	.2	22.5
.4	8.8	.4	12.2	.4	16.8	.4	22.7
.6	8.9	.6	12.4	.6	17.0	.6	23.0
.8	9.0	.8	12.5	.8	17.2	.8	23.3
						25.0	23.5

NOTE.—In cases where the tension rises .1 millimeter for a rise of .2°, the same pressure for the intermediate tenth degree may be taken as that given for the temperature immediately preceding it. Thus, for the temperature 10.1°, the tension 9.2 millimeters will be taken. For very accurate work, fuller tables given to the third decimal should be consulted.

In making the necessary correction for aqueous vapor, therefore, the number of millimeters of mercury representing the tension of aqueous vapor at that particular temperature at which the gas is measured, is deducted from the barometric pressure to which the gas is exposed. For exam-

ple, a gas is measured at 763 millimeters, and the temperature is 13.5°; then, by referring to Table 1, the tension at 13.5° is seen to be 11.5048 millimeters. Deducting this from the barometric pressure, we obtain 763 − 11.5048 = 751.4952 millimeters of true pressure.

If p stands for the pressure due to aqueous vapor, then the formula

$$V_0 = \frac{V(P-p)}{760(1+.003665\,t)}, \text{ or } \frac{V(P-p)\times 273}{760\times(273+t)} \qquad (4.)$$

expresses the necessary corrections to reduce a volume of gas, saturated with aqueous vapor, to the standard conditions.

22. When gases are confined over water, as in the gas burettes just described, the conditions of complete saturation with aqueous vapor are, of course, always present, and when mercury is employed as the confining liquid, complete saturation of the gas with aqueous vapor is insured by introducing a drop of water into the measuring tube. With this apparatus also, the gas volumes are always read at the atmospheric pressure, and, as the analytical operations are rapidly performed, changes of barometic pressure sufficient to influence the results need not be anticipated. Changes of temperature, however, must be guarded against as far as possible, and, with this object in view, it should be made an imperative rule never to handle the glass parts of gas analytical apparatus. In order to ascertain the temperature of the gas and see how far it is being maintained uniform throughout, a simple and convenient plan is to suspend a thermometer inside the level tube by means of a thread, so that it reaches nearly to the bottom, and remains there during the whole analysis. As the water is continually being passed backwards and forwards from the level tube to the measuring tube, the temperature of the gas may be taken as the same as that of the water over which it is confined, and, if the temperature of the latter does not materially change, that of the gas may be considered as practically uniform.

23. As previously stated, when conditions under which gas measurements are made are constant, it is not necessary

to reduce the observed volume to the standard conditions. This will be rendered more obvious from the following example:

The original volume of gaseous mixture in the burette measured 100 cubic centimeters at ordinary pressure (i. e., when the water was at the same level in both tubes). One constituent x was then removed by absorption and the gas measured again. Its volume now was 75 cubic centimeters at atmospheric pressure. The temperature was 16° and the barometric pressure 758 millimeters throughout.

Then (1) without making reduction to standard conditions, we obtain

$$100 - 75 = 25 = \text{percentage of } x \text{ in the mixture.}$$

(2) On reducing the two volumes by means of formula **4**,

$$V_0 = \frac{V(P-p)}{760(1+.003665\ t)},$$

we obtain

$$(a)\ V_0 = \frac{100 \times (758 - 13.5)}{760 \times (1.05864)} = 92.534.$$

$$(b)\ V_0 = \frac{75 \times (758 - 13.5)}{760 \times (1.05864)} = 69.276.$$

Therefore, $92.534 - 69.276 = 23.258$ = volume of x in 92.534 cubic centimeters of original gas, and

$$\frac{23.258 \times 100}{92.534} = 25 = \text{percentage of } x \text{ in the mixture.}$$

Since the tension of aqueous vapor is independent of pressure, then, in the event of any alteration of barometric pressure taking place during an analysis, it is only necessary to make a correction for pressure—not necessarily by reducing all the volumes to the standard, but by reducing all to the same pressure as any of them.

Thus, in the above, suppose that between the two measurements the barometer fell from 758 to 752 millimeters, the temperature remaining constant at 16°, then the following are the data:

Original volume = 100 c.c. at 16° and 758 mm.

After absorbing x, volume = 75 c.c. at 16° and 752 mm.

Then, $\frac{75 \times 752}{758} = 74.41$ = volume that the residual gas would occupy if measured under the same conditions as the original volume.

Hence, $100 - 74.41 = 25.59$ = percentage of x in the mixture.

If, now, from the above data, the two volumes be reduced to standard conditions by means of formula **4,** it will be found that the same result is obtained, namely, 25.59 percentage of x.

Again, since the tension of aqueous vapor depends on the temperature, increasing with the rise of temperature, change of temperature will obviously produce an alteration of the pressure, even though the barometric pressure remains constant. For example, suppose, in the above illustration, the 100 cubic centimeters of original volume are measured at 16° and the 75 cubic centimeters of residual gas are measured at 20°, the barometer standing uniformly at 760 millimeters, then the actual pressure in the first case is 760 − 13.5 (tension of aqueous vapor at 16°), and in the second it is 760 − 17.4 (tension at 20°).

Hence, if any change of temperature is observed in the gas during the progress of an analysis, the observed volumes must be reduced to the standard by means of formula **4,**

$$V_0 = \frac{V(P-p)}{760(1+.003665\,t)}.$$

24. Collection of Gas for Analysis.—If the gas for analysis is collected in the laboratory, as, for instance, a sample of ordinary illuminating gas, it may be introduced into the burette by first placing the measuring tube on a higher level than the level tube, and allowing the former to empty. By means of the three-way cock, shown in Figs. 5 and 6, communication between the measuring tube and the outer air is then opened, and a rapid stream of the gas passed through the tube from the top, until the air has been entirely swept

out. The upper tap is then closed and the lower one turned so as to reestablish communication with the level tube.

When the available supply of gas is comparatively small, it may be collected in a glass tube over water (or, if necessary, over mercury), and afterwards transferred to the burette, as described below. The tube may conveniently have the form shown in Fig. 7. It is first filled with water by sucking the liquid up and closing the rubber tube with a pinch cock, and the gas is then passed up from below in the usual manner. The tube is then connected to the gas burette, with the same precautions against enclosing air in the joints, as given below. When the gas is collected away from the laboratory, it should be taken in glass tubes drawn out to a capillary constriction at each end. These tubes are filled either by aspirating the gas through them so as to sweep out the air, and then hermetically sealing them at the constriction, or by taking them to the spot in a vacuous and sealed condition, and then breaking open one end in the gas to be collected. After the gas has filled the tube, the end is again hermetically sealed by means of a blowpipe.

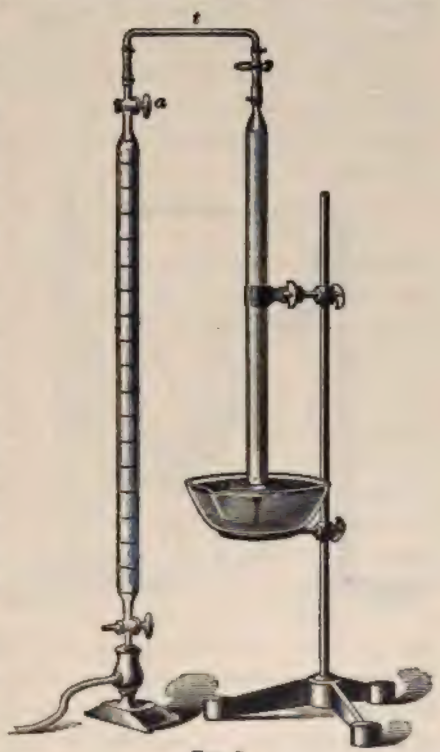


FIG. 7.

In order to transfer the gas from the sealed tube to the burette, a piece of capillary tube *t*, bent twice in right angles, is attached to the latter, as shown in Fig. 7, the joints

being wired round. The level tube is then raised, until water completely fills the measuring tube and drops from the open end of the bent capillary. Whenever the available supply of the gas to be analyzed renders such a course possible, the water used in the burette should be first saturated with the gas by shaking a quantity of water with some of the gas in a stoppered bottle for a few minutes. Near each end of the sealed tubes, a slight scratch with a file is made. Over one end, a short piece of rubber tube is slipped, and the projecting portion of it filled up with water. The bent capillary, already entirely filled with water, is then introduced into this tube, and the latter secured with binding wire. In this way, all air is excluded from the joint. The lower end of the tube is dipped into a vessel of water. The tube is broken at the file mark within the rubber joint, and the end beneath the water is also broken off by means of a pair of pliers. On lowering the level tube and opening the stop-cock a at the top of the measuring tube, the gas will be drawn over into the burette.

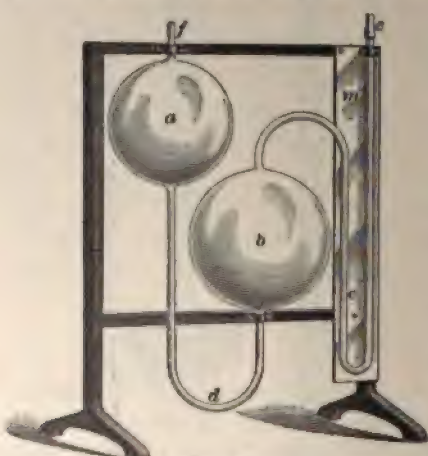


FIG. 8.

25. Absorption of Gases. — Except when the absorbing liquid is water, in which case the absorption would be made directly in the measuring tube of the burette, the absorption of the gases in a mixture is carried out in a separate piece of apparatus known as *absorption pipette*. The *simple absorption pipette* shown in Fig. 8 consists of two glass globes a and b; the capacity of b should be at least 150 cubic centimeters, so that when the gas from the full burette (100 cubic centimeters) is transferred to it, sufficient room remains for

an adequate quantity of the reagent. The two globes are connected by means of a bent glass tube *d*, and are fastened to a wooden stand to prevent breakage. A capillary tube *c* passes from the globe *b* before a plate of milk glass *m*, which is let into the wooden stand, in order to be able to trace readily the movements of the liquid thread in the capillary tube *c*. The exit tube *f* of the globe *a* and capillary tube *c* extend above the wooden frame; a small rubber tube *e* is connected to the protruding tube *c* and fastened by means of wire, and the tube furnished with a pinch cock. The reagent to be used is poured in at *f* (for which purpose a thistle funnel should be used to avoid spilling the reagent over the outside), filling the globe *b* entirely, *a* only partially, and the capillary tube *c* to the junction with the rubber tube near *e*. When not in use, *f* is closed by a cork and *e* by a glass rod, not with the pinch cock, which spoils the rubber tube after a short time. A separate pipette is used for each reagent, and a label designating the contents of the pipette should be attached to the wooden frame of each.

26. Manipulation of Single-Absorption Pipette.—To analyze a gas with the single-absorption pipette, the burette is filled with distilled water that has been previously saturated by shaking with the gas in question. The pipette is so filled with the absorbent that the bulb *a*, Fig. 8, remains empty. The absorbent must also be saturated, by shaking with gases that are but slightly soluble in it. The saturation of liquids is best done in a flask half filled with the reagent, a rapid stream of gas being led through the liquid, and the flask vigorously shaken. In technical work, where the same analyses are repeatedly made, the absorbent is kept saturated through continual use.

If the pipettes have the temperature of the room, as can be readily determined by introducing a thermometer at *k*, Fig. 9, the analysis is begun by drawing gas into the measuring tube in the manner described in Art. **16.** It is convenient to use exactly 100 cubic centimeters, so that the results in percentage may be read off directly. The

apparatus is now arranged as shown in Fig. 9. The pipette is placed on a wooden stand and is connected with the burette by the capillary tube *F*, which is a piece of ther-

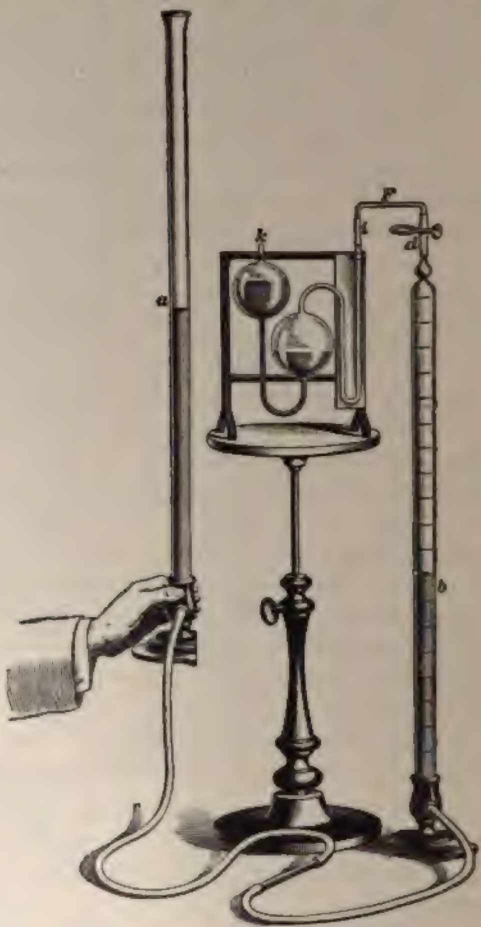


FIG. 9.

mometer tubing having a bore of .5 millimeter. To avoid the enclosing of air bubbles, the rubber tube *d* is first filled with water by means of a funnel, and the capillary *F* is then introduced. *F* is thus completely filled with water. The

rubber tube *i* of the pipette is squeezed between the thumb and the first finger of the right hand, and, while thus compressed and free from air, the capillary connecting tube is inserted. On raising the level tube *a* and opening the pinch cock at *d*, the gas passes through the connecting tube into the absorption pipette. Any small air bubbles that may have been enclosed when *F* was inserted into *i* are, at the beginning, separated from the gas by the water in *F*. If these bubbles do not take more than 5 to 10 millimeters of space in the capillary of the pipette, they may be disregarded, since the error arising therefrom is only about .03 cubic centimeter.

If the bubbles are larger, although after a little practice this will seldom occur, the gas is brought back into the burette by lowering the level tube, and the operation is repeated. When the gas has passed over into the pipette, about ½ cubic centimeter of water is allowed to follow, this water serving to rinse the capillary and to free it sufficiently from the absorbing liquid that it previously contained. The gas is now enclosed between two columns of liquid, the absorbent on the one side and the water in the capillary on the other side. The burette, having been closed by the pinch cock, is disconnected, and the pipette is carefully shaken and the absorption of the gas thus effected. The burette and pipette are then reconnected, the level tube is placed on the floor, and the gas is brought back into the burette, care being taken that *none* of the absorbing liquid passes further than the connecting capillary *F*. The pinch cock is closed, and the reading of the remaining volume is made.

27. Double, or Compound, Pipette.—In cases where it is necessary to prevent the reagent from coming into contact with atmospheric air (as, for instance, with alkaline pyrogallol, cuprous chloride, etc.), the *double*, or *compound*, *pipette*, shown in Fig. 10, is used. It differs from the pipette shown in Fig. 8, by having two extra bulbs, which, being partially filled with water, serve as a water seal and thus

prevent the reagent from coming in contact with the air. The apparatus consists of the large glass bulb *a*, of about 150 cubic centimeters capacity, and three smaller bulbs *b*, *c*, *d*, each having a capacity of about 100 cubic centimeters.

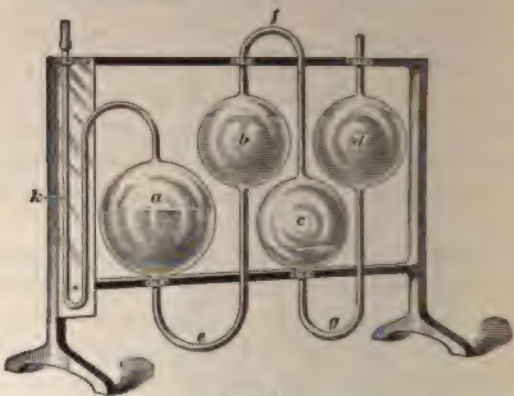


FIG. 10.

They are connected by the bent tubes *e*, *f*, and *g*, and end in the bent capillary tube *k*.

The addition of these two extra globes makes it somewhat more difficult to fill this pipette. It is necessary to so arrange matters that, when the absorbing reagent fills the bulb *a*, the water shall occupy *c*, so that, when the reagent passes up into *b*, the water shall be driven into *d*. If this condition is not properly secured, as the reagent is made to pass backwards and forwards between *a* and *b*, air will either be drawn in through the water in the water seal, or else some of the water itself will be drawn over into *b*.

28. Filling the Double-Absorption Pipette.—The following is considered the best method of filling the apparatus: The empty pipette is supported in an inverted position, and an ordinary 10-cubic-centimeter pipette *p* is connected to the capillary tube *k*, as shown in Fig. 11. To the free end of the latter, a piece of narrow glass tube *t* is attached by means of a short piece of rubber tubing provided with a pinch cock *l*. Another short length of rubber tube

also carrying a pinch cock *n*, is attached to *m*. The air within the apparatus is then swept out by passing a stream of

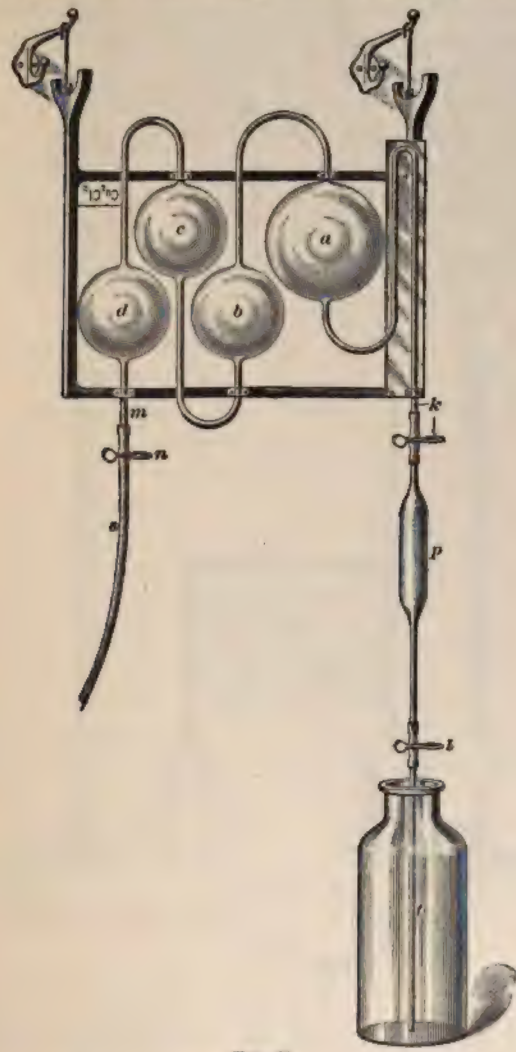


FIG. 11.

some inert gas (i. e., inert toward the particular reagent that is destined to fill the pipette), such as nitrogen or carbon

dioxide, for instance. The narrow glass tube *t* is then dipped into the bottle containing the reagent in question, which is drawn up into the apparatus by applying suction through the rubber tube *s*. As soon as the globe *a* is completely filled, care being taken not to draw any liquid over into globe *b*, the clamps *n* and *l* are closed, and the tube *t* disconnected.

The apparatus is returned to its normal position, the little pipette *p* being supported by the hand. The burette, which has been previously filled with the same inert gas used for the pipette, is now attached to the rubber union at *l* by means of the bent capillary tube *t*, as shown in Fig. 12. The

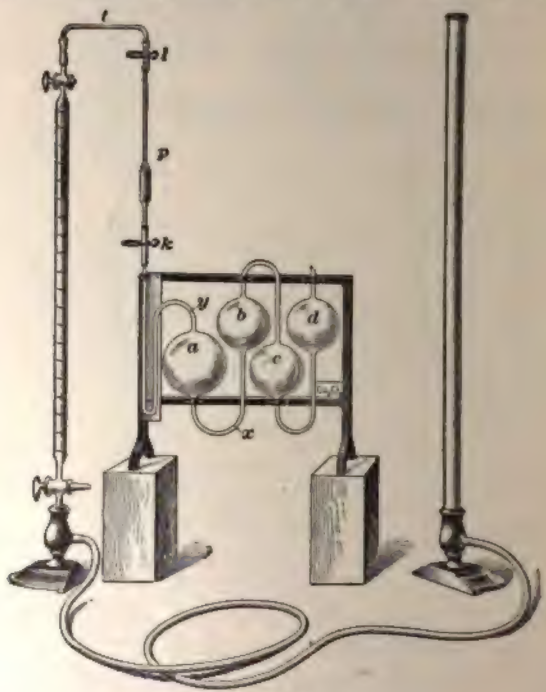


FIG. 12.

reagent should now occupy the entire space between the clamp *l* and a point *x* in the bent tube, except probably for a small bubble that, most likely, will have collected at *y*. The rubber tube (see Fig. 11) is now removed, and 3 or

4 cubic centimeters of water are introduced into the globe *d* by means of a thistle funnel. This water will partly descend into the bent tube connecting *c* and *d*, and is intended to serve as a temporary water seal.

The inert gas in the burette is now slowly passed into the pipette by raising the level tube and opening the stop-cock of the measuring tube and the clamps *l* and *k*. As the gas passes in, the reagent is driven from the globe *a* to *b*, while the gas that was in *b* is expelled through the small quantity of water that was in *d*. When all the gas from the burette has been transferred to the pipette, clamp *l* is closed, and water is introduced into the globe *d* until it is nearly filled. The clamp *k* is now closed, and the little pipette *p* removed. The clamp should be opened again just to allow the liquids to sink to their natural level, and the rubber then closed by means of a plug or glass rod. The gas pipette is now properly charged, the space between the reagent and the water seal being occupied by inert gas, while the confining water occupies such a position in the globes *c* and *d* that it will neither pass over into *b* nor allow air to pass through when the reagent is being transferred backwards and forwards from *a* to *b*. The interposition of the 10-cubic-centimeter pipette in the filling operation will have secured the introduction of rather more than enough of the reagent to fill globe *a*. When, therefore, in the process of returning a gas from the absorption pipette to the burette, the reagent completely fills the bulb *a* and capillary tube, there will still remain a few cubic centimeters in globe *b*.

Since 100 cubic centimeters of gas (the capacity of the burette) may at any time be introduced into the globe *a*, it will be evident that the capacity of *b*, *c*, and *d* must not be less than this volume, otherwise they will overflow.

29. Gases Usually Estimated by Absorption.—The gases that are most frequently estimated by absorption in a simple gas pipette, and the reagents employed for this purpose are:

1. *Carbon Dioxide* CO_2.—This is absorbed by *potassium*

hydrate. Potassium hydrate of a suitable strength to serve as reagent in gas analysis is made up by dissolving 150 grams of caustic potash in 500 cubic centimeters of water. The pipette shown in Fig. 8 is used for the determination.

2. *Carbon Monoxide CO.*—The absorption agent used is *cuprous chloride.* Cuprous chloride being soluble in ammonia as well as in hydrochloric acid, either an acid or an ammoniacal solution may be used. The former is preferable, except under certain circumstances, which are described in Art. **48**, when the ammoniacal solution has to be used. The reagent is made up as follows:

(*a*) *Acid Solution.*—Thirty grams of chemically pure cuprous chloride are added to 50 cubic centimeters of water in a flask, and 150 cubic centimeters of strong hydrochloric acid are added. A few copper turnings or thin strips of copper may be placed in the brownish solution, and the flask corked up for a day or two, when the liquid will become colorless.

(*b*) *Ammoniacal Solution.*—Twenty grams of cuprous chloride are mixed with 150 cubic centimeters of water in a flask fitted with a perforated cork carrying two tubes, one reaching to the bottom, while the other ends just below the cork. The air is swept out of the flask by a stream of indifferent gas, such as hydrogen or carbon dioxide, after which the exit tube is made dip beneath the water. A stream of ammonia is then passed into the solution (obtained by gently heating a strong solution of ammonia in a separate flask, the latter not being connected until the issuing ammonia has expelled the air) until the cuprous chloride has entirely dissolved. Any unnecessary excess of ammonia should be, however, avoided. This reagent is used in the double pipette, shown in Fig. 10, and care must be taken to expose the reagent as little as possible to the atmosphere while filling the pipette (see Art. **28**).

3. *Oxygen.*—Oxygen is absorbed by *alkaline pyrogallol.* The reagent is prepared by dissolving 20 grams of pyrogallol $1:2:3 = C_6H_3(OH)_3$ in 200 cubic centimeters of a potassium-hydrate solution having the same strength as that used for the absorption of carbon dioxide.

4. *Hydrocarbons* (*olefines*).—Hydrocarbons are absorbed by fuming *sulphuric acid* or *bromine water*. After exposure to either of these reagents, the gas is freed from either sulphur dioxide or from the vapor of bromine by being transferred to another pipette containing potassium-hydrate solution. The tubes of the pipette containing fuming sulphuric acid as reagent must be kept closed by means of a piece of glass rod and rubber tube, when the apparatus is not used.

Benzene vapor is absorbed by sulphuric acid, but not by bromine water. It is also absorbed by fuming nitric acid.

5. *Nitric Oxide*.—Nitric oxide is absorbed by *ferrous sulphate*. The ferrous sulphate is prepared by dissolving 70 grams of ferrous sulphate in 150 cubic centimeters of water. A double pipette is used for this determination. In case a double pipette is not at hand, the absorption can be made in a single pipette, but then, instead of ferrous sulphate, a solution of potassium permanganate, acidified with sulphuric acid, must be employed as absorption agent.

6. *Chlorine*, *hydrogen sulphide*, *sulphur dioxide*, *hydrochloric-acid gas*, and other acid gases are generally absorbed from gaseous mixtures by potassium hydrate.

ABSORPTION OF A GASEOUS MIXTURE.

30. As a first exercise in manipulating gas apparatus, it is recommended to make an absorption of a carefully prepared mixture of gases. A mixture of carbon dioxide, oxygen, carbon monoxide, and nitrogen are especially suitable for this purpose, as these gases are constantly met with, associated together in such gaseous mixtures as furnace gases, generator gases, coal gas, water gas, etc.

The mixture is prepared by partially filling (say, about three-fourths) a collection tube similar to that shown in Fig. 7 with air. A small quantity of oxalic acid is heated with strong sulphuric acid in a test tube fitted with a cork and delivery tube, and the mixture of CO and CO_2 thus obtained is collected in the collection tube, previously mentioned, so

as to fill the remaining one-fourth. The tube now contains a mixture of the four gases, oxygen and nitrogen in the air, and CO and CO_2 collected from the decomposed oxalic acid. It will be obvious that the order in which the gases are to be absorbed from a mixture deserves careful consideration, as, for instance, in this case, the oxygen must be absorbed before the carbon monoxide, otherwise the reagent used to absorb the latter gas (cuprous chloride) would be acted on by the oxygen present.

The different gases should be estimated in the following order:

Carbon dioxide, absorbed by means of potassium hydrate.
Oxygen, absorbed by means of pyrogallol.
Carbon monoxide, absorbed by means of cuprous chloride.
Nitrogen, estimated by difference.

31. Preparation of Water Used in Gas Burette.—The water that is used in the gas burette has to be saturated with the gaseous mixture to be analyzed before beginning the analysis, in order to prevent absorption of the mixture during the analysis, and thus obviating the exactness of the result. For this purpose, a stoppered bottle holding about 300 or 350 cubic centimeters is filled with distilled water and inverted in a water trough. About 100 cubic centimeters of the gaseous mixture is bubbled up into the bottle, which is then closed with the stopper, and the gas thoroughly shaken with the remaining water for a few minutes.

Some of this saturated water is poured into the level tube of the gas burette, and the stop-cock at the foot of the measuring tube is turned so as to establish communication between the two tubes. It should be remarked here that this stop-cock must not be touched again through the entire process of the analysis, the passage of the gas to and from the measuring tube and the various pipettes used being entirely controlled by the upper stop-cock of the measuring tube. The bent capillary connecting tube is then attached to the top of the measuring tube, and the latter is completely filled with water by raising the level tube and opening the

stop-cock at the top of the measuring tube, until the liquid drops from the end of the capillary tube. The rubber connection on the collecting tube containing the gas is filled up with a drop of water and joined to the end of the bent capillary (see Fig. 7) and the connections secured with thin binding wire. The level tube is lowered and the pinch cock on the collecting tube and the upper stop-cock of the measuring tube are opened, whereby gas is drawn over into the latter tube. When sufficient gas has thus been transferred, the pinch cock and stop-cock are closed, and the two tubes disconnected. One minute is allowed to elapse for the water to drain down the walls of the measuring tube, when the volume of the gas introduced is read off by lowering the level tube until the level of the water in it and in the measuring tube is the same. The graduation mark that coincides with the bottom of the meniscus represents the volume of gas taken for the analysis.

32. It is convenient to employ, when possible, exactly 100 cubic centimeters of the gas under analysis, in which case the number of cubic centimeters of the various constituents that are absorbed represents the percentage of each ingredient in the gas mixture. If, therefore, more than 100 cubic centimeters have first been introduced into the apparatus, the excess may be removed by raising the level tube until the gas is compressed to exactly 100 cubic centimeters, then, keeping the water in that position by pressing a finger upon the rubber tube, the stop-cock at the top is momentarily opened. This allows the excess of gas to escape, leaving exactly 100 cubic centimeters at atmospheric pressure. This is controlled by again lowering the level tube until the water in each tube is at the same level, when the gas should be found to occupy 100 cubic centimeters.

33. Determination of Carbon Dioxide.—We are now ready to begin the first determination, that is, that of carbon dioxide, and, for this purpose, the burette is attached to the absorption pipette, containing potassium hydrate, in the

manner shown in Fig. 13. Before the two pieces of apparatus are, however, joined, the potassium hydrate solution is drawn up so as to completely fill the globe *a*, and the bent capillary tube to the mark *c*, which is made on the white plate behind it. The pinch cock keeps it in this position. After the rubber connections have been secured with

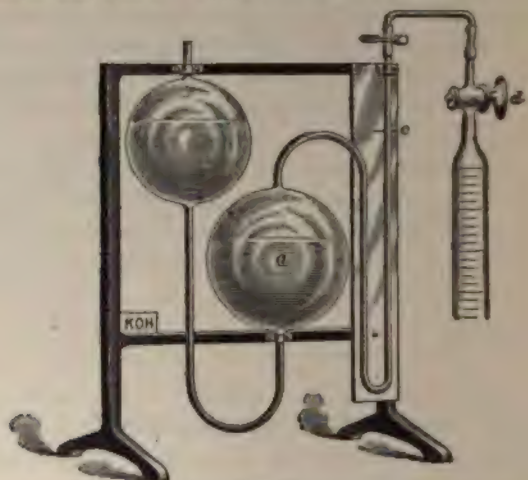


FIG. 13.

binding wire, the pinch cock is opened, when, if the joints are tight, the reagent will not sink from its position at *c*. The pinch cock may be kept open by lifting it so that it nips the glass tube. The level tube is now raised (being handled exclusively by its foot) and the stop-cock *d* at the top of the measuring tube is opened.

The gas is thus transferred completely to the bulb *a* of the pipette; 2 or 3 drops of water from the measuring tube are allowed to follow the gas into the bulb (by doing so, the capillary tube of the pipette is washed each time the apparatus is used), after which the stop-cock *d* is closed. The gas is allowed to remain in contact with the potassium-hydrate solution for about 5 minutes, during which time the apparatus is gently shaken so as to moisten the sides of the globe with the reagent. The level tube is again lowered and the stop-cock *d* opened, and thus the gas returned to the measuring

tube. As soon as the potassium-hydrate solution reaches the point in the capillary tube opposite *c*, the stop-cock is closed.

The utmost care should be exercised not to allow the reagent to come in contact with the rubber connections, or to pass into the measuring tube. The pressure tube is then held in such a position that the water stands at an equal level in both tubes, and, after waiting 1 minute for the water to drain down the walls of the tube, the volume that the gas now occupies is read off.

The operation of filling the pipette with the gas is once repeated in exactly the same way as previously described, in order to be sure that all the carbon dioxide has really been absorbed by the reagent, and the volume is again read off at atmospheric pressure. If the two readings agree, the first absorption was complete. For example,

Original volume of gas	= 1 0 0 c.c.	
Volume after absorption by KOH	= 8 8 c.c.	
Carbon dioxide	= 1 2 c.c.	= 12%.

34. Determination of Oxygen.—The potassium-hydrate pipette is now detached from the bent capillary tube at the joint immediately above the pinch cock Fig. 13, and replaced by the double pipette containing the alkaline solution of pyrogallol. Before the latter is connected, the reagent is drawn up into the capillary tube to a marked point, which is, as nearly as possible, the same distance from the pinch cock as that on the pipette used for the previous determination. The gas is transferred for absorption exactly as in the former case, and is left in contact with the reagent, with occasional gentle shaking, for 10 minutes. It is then returned to the measuring tube, the same care being taken to bring the reagent exactly to the mark on the capillary tube. The stop-cock is closed, and, after allowing time for the water to drain off the walls of the measuring tube, the volume of the residual gas is read off at atmospheric pressure. For example,

Volume of gas before absorption of oxygen	= 8 8 c. c.	
Volume of gas after absorption of oxygen	= 7 3 c. c.	
Oxygen	= 1 5 c. c.	= 15%.

35. Determination of Carbon Monoxide.—After finishing the determination of oxygen as described above, the double pipette containing the pyrogallol is disconnected, and replaced by one containing cuprous chloride in acid solution, the reagent being previously drawn over into the capillary tube to a mark in the same relative position as in the two previous cases. The gas is transferred to the pipette and allowed to remain exposed to the reagent; after the lapse of 10 minutes, it is retransferred to the measuring tube of the burette, and its volume determined as previously stated. For example,

Volume of gas before absorption of carbon monoxide	= 73 c. c.
Volume of gas after absorption of carbon monoxide	= 60.5 c. c.
Carbon monoxide	= 12.5 c. c. = 12.5%.
Volume of residual gas (nitrogen)	= 60.5 c. c. = 60.5%.

Hence, the composition of the gas under examination is:

Carbon dioxide	= 12
Carbon monoxide	= 12.5
Oxygen	= 15
Nitrogen (by difference)	= 60.5
Total	= 100.0

A duplicate analysis was made, and the correctness confirmed.

ESTIMATION OF GASES BY COMBUSTION.

DETERMINATION OF HYDROGEN.

36. When hydrogen and oxygen combine according to the equation

$$2H_2 + O_2 = 2H_2O$$

the 2 volumes of hydrogen and 1 volume of oxygen practically cease to occupy space, since the volume of the condensed water is inappreciable. By measuring the contraction

of volume that takes place under these circumstances, and multiplying this by $\frac{2}{3}$, the volume of hydrogen that was burnt is determined.

The estimation of hydrogen is then accomplished by mixing a measured volume of the gas with a measured volume of air—rather greater than the volume estimated to be required to furnish the necessary volume of oxygen—and by causing the mixture of hydrogen and oxygen to unite by one of the methods described below. After the combination has been accomplished, the residual gas is again measured, and two-thirds of the contraction will represent the volume of the hydrogen consumed.

Two methods that are mostly used in practical analytical work are given below.

37. Combustion of Hydrogen by Means of Palladiumized Asbestos.—The hydrogen is mixed with an excess of the required volume of air in a gas burette that is attached to a single-absorption pipette charged with distilled water. The capillary tube that forms the connection between the absorption pipette and the measuring tube contains a thread of asbestos upon which has been deposited a quantity of finely divided palladium. As the gas is passed from the measuring tube of the burette to the pipette, it comes in full contact with the palladiumized asbestos (which is gently warmed by means of a small flame), and the hydrogen and oxygen are thereby caused to unite. The gas is finally returned to the burette and measured.

38. Preparation of Palladiumized Asbestos.—The capillary tube containing the palladiumized asbestos is prepared in the following manner: .25 gram of palladium foil is dissolved in as little aqua regia as possible in a small porcelain dish and the solution evaporated to dryness on the water bath. The residue is moistened with 3 or 4 drops of strong hydrochloric acid, and 1 cubic centimeter of water added. The mixture may be gently warmed to complete the solution. To this red-brown solution, when cold, 20 drops

of a cold saturated solution of sodium formate are added. Into this mixture, which will not exceed 2.5 cubic centimeters in volume, .25 gram of asbestos thread is immersed, which will soak up the whole of the liquid. It is self-evident that the thread must be sufficiently fine to admit of being pushed into a capillary tube of 1 millimeter bore. It may be obtained by unraveling a piece of asbestos cloth so as to get single strands. It is cleaned from grease by treating it once or twice with a little carbon disulphide in a test tube and then spreading it out on a clean piece of paper to dry, after which it should be heated for a few minutes on a piece of platinum foil. A quarter of a gram will be about 60 centimeters in length.

A strong solution of sodium carbonate is added by means of a dropper and gently worked into the soaked thread with a glass rod, until the mixture is alkaline, and the dish placed on a water bath. A gentle heat is sufficient to reduce the palladium, which is then precipitated throughout the asbestos as a black deposit. When the contents of the dish are dry, they are rinsed 3 or 4 times with hot water, in order to dissolve out any soluble salts. The thread is then removed and cut into short pieces, each about 4 centimeters long. One of these pieces is straightened out by a gentle twisting of the fingers, and laid on a piece of blotting paper for a few minutes, to remove any superfluous water. It is then introduced into a thick-walled capillary tube, 1 millimeter bore and about 15 centimeters long. When the thread has been pushed a little way into the tube, it may readily be drawn into the middle by applying a gentle suction to the other end. The thread is then dried by gently warming the tube and slowly drawing air through it, after which the tube is bent at right angles, about 3 centimeters from each end. The same piece of palladiumized asbestos may be used for several combustions.

39. Analysis of a Gaseous Mixture of Hydrogen and Air.—As an exercise of this analysis, a mixture of hydrogen and air may be conveniently employed. About

20 cubic centimeters of pure hydrogen are introduced into the gas burette, and the volume accurately measured. The level tube is then lowered, and a quantity of air introduced into the burette until the total volume amounts to between 80 and 85 cubic centimeters; or, in other words, about 60 to 65 cubic centimeters of air are added, and the volume is again accurately measured.

The gas burette is now attached to a single gas pipette charged with water by means of the capillary combustion tube containing the palladiumized asbestos prepared according to Art. **38,** instead of the usual connecting tube. The palladium is gently heated by moving a Bunsen flame along the tube, which must be kept warm through the entire operation, so as to prevent water, the product of the combustion of hydrogen and oxygen, from condensing in it. The temperature of the tube, however, must not approach a visible redness. The gas is allowed to pass slowly over the warm palladium, which will be seen to glow at the end toward the incoming gas. When the entire volume of the gas has been passed over into the pipette, it is slowly drawn back again into the burette. This process is repeated once or twice, although, if the palladiumized asbestos is in good order, one repetition is usually sufficient, after which the residual gas is measured. It is then passed once more into the pipette, and back, and measured again. If the two measurements agree, the process is complete. For example,

Original volume of hydrogen taken	= 20.5 c. c.
Excess of air	= 63.3 c. c.
Total volume of mixture	= 83.8 c. c.
Volume of combustion	= 53.2 c. c.
Contraction	= 30.6 c. c.

$30.6 \times \frac{2}{3} = 20.4$ c. c. = volume of hydrogen found.

40. For the analysis of marsh gas and similar hydrocarbons, some chemists prefer the apparatus shown in Fig. 14, and which is based on the occlusion of hydrogen by palladium black. The gas burette *A* and the absorption pipette *B*

are joined together by means of the capillary tubes *e*, *e* and the tube *h*. This tube *h* is about 4 millimeters internal

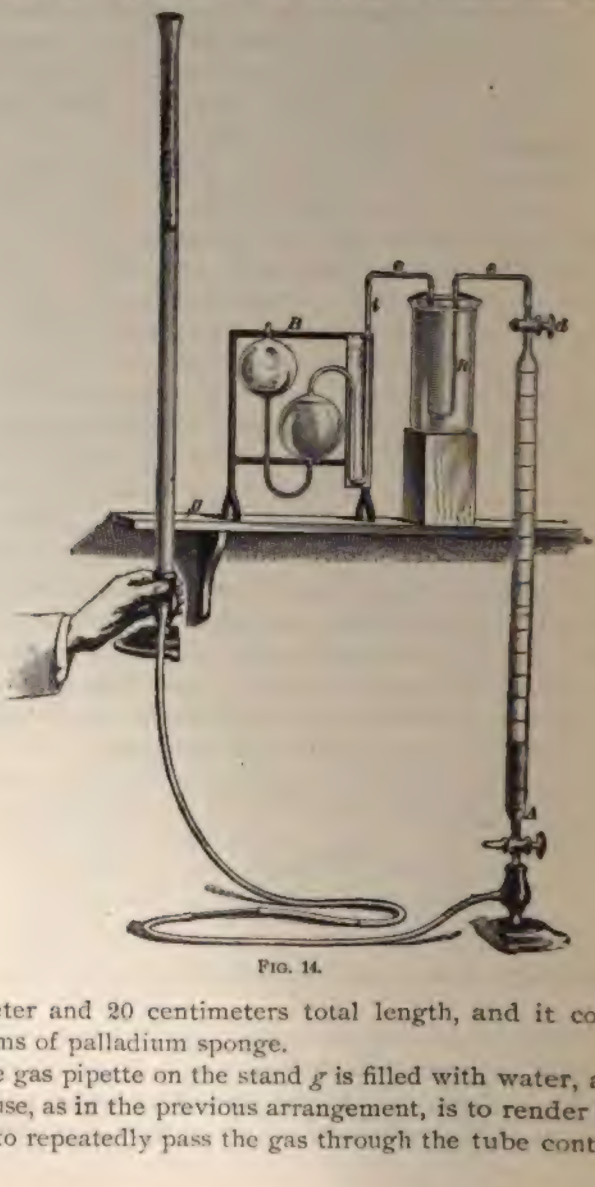


FIG. 14.

diameter and 20 centimeters total length, and it contains 4 grams of palladium sponge.

The gas pipette on the stand *g* is filled with water, and its only use, as in the previous arrangement, is to render it possible to repeatedly pass the gas through the tube containing

the palladium. To determine the amount of hydrogen in a gaseous mixture, the gas is measured in the burette joined to the pipette *B*, which is filled with water nearly to *i*. The tube *h* is placed in a good-sized beaker containing water of from 90° to 100°, and, after opening the stop-cock *d*, the gas is driven 3 or 4 times back and forth through the palladium by raising and lowering the level tube.

The hot water is then replaced by water of the temperature of the room, and the gas is again passed twice through the **U** tube, in order to cool it completely. On drawing the gas so far back into the measuring tube that the water in the pipette again stands near *i*, the gas is measured, and the difference between the two measurements, made before and after the absorption, corresponds to the hydrogen plus the amount of air enclosed in the **U** tube when the apparatus was put together. This air volume, with its oxygen contents, may be determined with sufficient exactness once for all by closing, with a piece of rubber tube and glass rod, one side of the tube filled with palladium, cooling the tube to about 9° by placing it in cold water, and then, after connecting it by a capillary with a gas burette completely filled with water, warming it to 100° by placing it in boiling water. The expansion of the enclosed air volume corresponds to a difference of temperature of 91°, i. e., to a third of the enclosed volume of gas.

The palladium is regenerated after the reaction by first leading air over it, whereby it becomes quite hot, removing any drops of moisture that may collect, so that the palladium may easily be shaken out in the form of a dry powder, and then superficially oxidizing the metal by heating it on the lid of a platinum crucible.

41. Combustion of Hydrogen by Explosion With Air.—For this purpose, the mixture of hydrogen with excess of air is transferred to a special piece of apparatus known as an *explosion pipette*, in which are sealed two pieces of platinum wire, whereby the gaseous mixture may be ignited by a spark from a Ruhmkorff coil. One form of these explosion pipettes, in which the gas is confined over water, is shown in

Fig. 15. Water that has been acidulated with sulphuric acid and boiled to expel any dissolved gases is introduced at *a* until the bulb *b* is just full, and the liquid stands level in the other limb. On the tubes *a* and *e*, pieces of thick-walled rubber tubes are securely wired, and a pinch cock is placed on each. At *d*, two platinum wires are sealed into the glass, between which the electric spark is passed when the gas is to be exploded. In the lower part of the tube at *c*, two platinum electrodes are fused into the glass. These are for the purpose of adding a small quantity of electrolytic gas to the mixture, when the proportion of combustible gas is so small that no explosion will take place when the electric spark is passed.

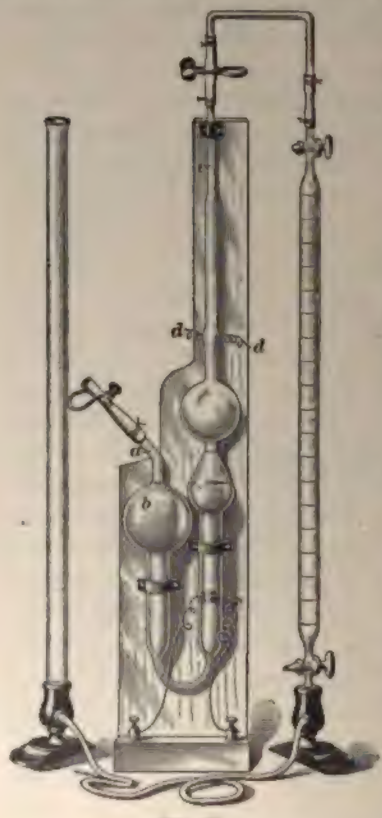


FIG. 15.

Before the electrolytic gas is generated, the mixture under analysis is transferred to the measuring tube, which is then detached from the explosion pipette. The two wires from a battery, not from the coil, are then connected to the electrodes *c* and the oxygen and hydrogen that is evolved is allowed to escape. The current is allowed to pass for about 15 minutes, in order to saturate the water, after which the current is stopped and the liquid driven up to the usual mark on the capillary. The burette is reconnected and the gas returned to the pipette. A small quantity of electrolytic gas is then generated, and thoroughly

mixed with the gas already present before exploding. It is not necessary to know the volume of the gas thus added, as it entirely disappears when fired.

42. As a first exercise in the use of an explosion pipette, a mixture of pure hydrogen and air may be advantageously employed. About 10 to 15 cubic centimeters of hydrogen are introduced into the gas burette, and, after being exactly measured, about 60 to 70 cubic centimeters of air are added, and the mixed gases again measured. The burette is then attached to the explosion pipette, the liquid in the latter being previously drawn up to a mark on the capillary tube *e*. The gas is then passed over into the pipette, and the clamps on the rubber tubes are both closed. The wires from the induction coil are attached to the wires at *d*, and the electric spark allowed to pass. The explosion, although not at all violent, will cause a momentary expansion within the apparatus, but, if sufficient liquid is present, no gas will be driven out of the bulb tube. The thick rubber tube on *a* being closed, the small quantity of air that is in the bulb *b* serves as a cushion, so to speak, at the moment of the explosion, and thus relieves the other part of the apparatus from undue pressure. The moment after passing the spark, the tube *a* is opened, and then the gas is returned to the burette and measured. The contraction represents the hydrogen and atmospheric oxygen with which it has combined to form water, and two-thirds of this shrinkage is the volume of hydrogen that was present. For example,

Volume of hydrogen taken	= 12.5 c. c.
Volume of air	= 63.3 c. c.
Volume of hydrogen and air	= 75.8 c. c.
Volume after explosion	= 57.5 c. c.
Contraction	= 18.3 c. c.

$18.3 \times \frac{2}{3} = 12.2$ c. c. = volume of hydrogen found.

43. For practice in the use of electrolytic gas, the following experiment is recommended: A quantity of air, say 55 or 60 cubic centimeters, is introduced into the burette, and its volume measured in the usual way. The current from

four or five Grove's cells, or its equivalent from any other source, is passed through the dilute acid in the explosion pipette by means of the electrodes at *c*, Fig. 15, for about 10 minutes, and the liquid shaken up once or twice with the gas in order that it may become saturated. The current is then turned off and the liquid drawn up to the mark on the capillary. The burette containing the measured volume of air is attached in the usual manner. About 12 cubic centimeters of electrolytic gas are then generated in the pipette and drawn over into the burette. The actual amount of electrolytic gas that has been added may be ascertained by measuring the total volume of gas in the burette. It is not necessary, however, to know this volume exactly, and a very little practice will enable the student to estimate the volume by the space it occupies in the explosion pipette as it is generated. The mixture of air and electrolytic gas is then passed twice backwards and forwards from the burette, to insure a complete mixing, after which the clamps are closed and the mixture exploded. The residual gas is transferred back to the burette and measured, when the volume should be exactly the same as previously introduced.

Usually, after the first experiment, the volume of the residual air is not exactly identical with that originally taken, owing to the imperfect saturation of the liquid with the various gases. If this is the case, a similar quantity of electrolytic gas should again be added, and the mixture exploded once more after thorough admixture. The volume of the residual gas after this second explosion should then exactly agree with that which was measured after the first operation. The process may be repeated with varying amounts of electrolytic gas, and the volume of the residue will be found to remain constant.

DETERMINATION OF MARSH GAS.

44. Explosion of Marsh Gas Over Water.—The product of an explosion of marsh gas (methane) and air is carbon dioxide and water, as is seen from the subjoined equation:

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$

The equation shows that if methane is exploded with air, the volume of CO_2 obtained is equal to the original volume of marsh gas present, and also that 3 volumes present before the explosion are reduced to 1 volume, that of CO_2, after the explosion. The contraction, therefore, is two-thirds of the original volume of the reacting gases; or, in other words, the contraction is equal to twice the carbon dioxide produced, or to twice the volume of marsh gas exploded.

Owing to the effect of pressure in increasing the solubility of carbon dioxide in water, it is only possible to obtain accurate results when mercury is used as the confining liquid.

45. Determination of Loss of Carbon Dioxide by Solution.—With a view to ascertaining the extent of the loss of carbon dioxide by solution in water, when the explosion is performed over that confining medium, the following experiments were made with the apparatus shown in Fig. 14:

1. 67 cubic centimeters of a mixture of air and carbon dioxide, containing 9 per cent. CO_2, were introduced into the apparatus and 12 cubic centimeters of electrolytic gas added. After explosion, the remaining volume occupied 66.7 cubic centimeters.

$$\text{Loss of } CO_2 = .3 \text{ c. c.} = .4\%.$$

2. 78 cubic centimeters of a similar mixture, containing 20 per cent. CO_2; 15 cubic centimeters electrolytic gas added. Volume after explosion = 77.2 cubic centimeters.

$$\text{Loss of } CO_2 = .8 \text{ c. c.} = 1\%.$$

3. 50.8 cubic centimeters of a similar mixture, containing 40 per cent. CO_2; 15 cubic centimeters electrolytic gas added. Volume after explosion = 49 cubic centimeters.

$$\text{Loss of } CO_2 = 1.8 \text{ c. c.} = 3.3\%.$$

About the same volume of electrolytic gas was added 3 times, and the mixture exploded and measured after each addition; the volumes obtained were 47.4 cubic centimeters, 46.2 cubic centimeters, and 45.2 cubic centimeters, showing a fairly regular loss of carbon dioxide.

4. 47.2 cubic centimeters of air containing 36.4 per cent of CO_2.

(a) 20 c. c. electrolytic gas added; after explosion volume = 45.6 c. c.

(b) 12 c. c. electrolytic gas added; after explosion volume = 45.0 c. c.

(c) 20 c. c. electrolytic gas added; after explosion volume = 43.6 c. c.

(a) loss = 1.6 c. c., or 3.4%

(b) loss = 0.6 c. c.

(c) loss = 1.4 c. c.

Experiments 1, 2, and 3 show that with about the same force of explosion, the loss of CO_2 increases as the percentage rises, while experiment 4 shows that with the same percentage of carbon dioxide, the amount absorbed depends on the force of the explosion.

46. Explosion of Marsh Gas Over Mercury.—An explosion pipette in which mercury is employed is shown in Fig. 16. It differs from the ordinary absorption pipette only in containing two platinum wires fused in the upper part of bulb *a*, and being furnished with a stop-cock *c*, in order to close the communication between the two bulbs. Before the apparatus is connected to the burette containing the measured mixture for explosion, the mercury is driven over into the capillary tube to a fixed mark by blowing through the rubber tube on the upper bulb *b*, and, similarly, when the gas is transferred from the burette to the explosion

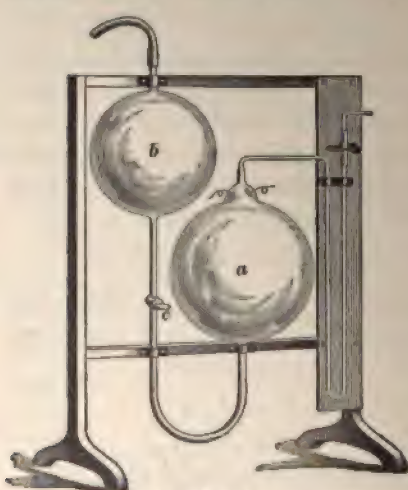


FIG. 16.

pipette, it must be drawn over by applying suction to the same rubber tube. The water from the burette should be made follow the gas so as to just fill the capillary tube, but without being allowed to enter the bulb. Before exploding the mixture, both the pinch cock and stop-cock are closed. After the explosion, the gas is transferred to the burette and measured. The explosion pipette is then disconnected and replaced by the simple-absorption pipette containing potassium hydrate, and the carbon dioxide is absorbed in the usual way.

47. Analysis of Mixtures of Hydrogen, Methane, and Nitrogen.—Many gaseous mixtures that constantly come under analysis (such as coal gas, producer gas, water gas, blast-furnace gases, etc.), contain varying quantities of these three gases along with others. After all the other gases have been estimated by absorption in their respective reagents, the hydrogen and marsh gas in the residue are determined by one of the following methods, while the nitrogen is estimated by difference:

48. *First Method.*—The gas is mixed with an excess of air, and the hydrogen estimated by combustion, by means of palladiumized asbestos, as described in Art. **37.** Under these conditions the marsh gas does not burn. The marsh gas is then determined by exploding the residual mixture and absorbing the carbon dioxide produced, as previously described. The volume of nitrogen is found by deducting from the original volume of gas the hydrogen and marsh gas thus determined.

A description of an analysis performed by the writer will make the proceedings clear to the student.

To the action of the following reagents, 100 cubic centimeters of coal gas were exposed:

(*a*) Potassium hydrate, to absorb carbon dioxide.

(*b*) Alkaline pyrogallol, to absorb oxygen.

(*c*) Fuming sulphuric acid, to absorb olefines and benzene vapor.

(*d*) Ammoniacal cuprous chloride, to absorb carbon monoxide.*

The residual gas, measuring 86.6 cubic centimeters, was returned to the cuprous-chloride pipette, while the burette was disconnected and the water in it (previously saturated with coal gas) was replaced by water saturated with air. Then, 20 cubic centimeters of the gas were transferred to the burette (the rest being reserved for a subsequent experiment), and air was added in more than sufficient quantity for the complete combustion of the hydrogen.

Volume of gas = 20.0 c. c.
Volume of gas + air = 64.4 c. c.

This mixture was then passed over the palladiumized asbestos.

Volume after combustion of hydrogen = 48.2 c. c.
Therefore, $64.4 - 48.2 = 16.2$ c. c. = contraction,
and $16.2 \times \frac{2}{3} = 10.8$ = volume of hydrogen present in 20 c. c. of gas.

To the residual gas (consisting of marsh gas, nitrogen, and a small surplus of oxygen) an excess of oxygen was added.

Volume of residual gas = 48.2 c. c.
Volume of residual gas + air = 69.6 c. c.

The mixture was then exploded, and the carbon dioxide absorbed.

Volume after explosion = 52.8 c. c.
Therefore, $69.6 - 52.8 = 16.8$ = contraction.
Volume after absorption of CO_2 = 44.4 c. c.
Therefore, $52.8 - 44.4 = 8.4$ = volume of CO_2 produced.
Therefore,
8.4 c. c. = volume of marsh gas present in 20 c. c. of gas
20.0 c. c. $- (10.8 + 8.4) = .8$ c. c.
= volume of nitrogen in 20 c. c. of gas.

* When the absorption of carbon monoxide is to be followed by the combustion of hydrogen with palladiumized asbestos, the ammoniacal solution of cuprous chloride should be used.

Since the original volume of gas taken for analysis was 100 cubic centimeters,

then $$\frac{10.8 \times 86.6}{20} = 46.76\% \text{ of hydrogen,}$$

and $$\frac{8.4 \times 86.6}{20} = 36.37\% \text{ of marsh gas,}$$

and $$\frac{.8 \times 86.6}{20} = 3.46\% \text{ of nitrogen.}$$

49. *Second Method.*—By this method, to the mixture of hydrogen and marsh gas and nitrogen sufficient air or oxygen is added for the complete combustion of both combustible gases, and the mixture exploded. The contraction is then measured, after which the carbon dioxide is absorbed and the volume again measured. From these data, the volumes of the hydrogen and marsh gas can be calculated. As already explained in Art. **44,** the contraction due to the combustion of marsh gas is twice the volume of carbon dioxide; if, therefore, the volume of carbon dioxide is ascertained (by absorption with potassium hydrate), and twice this volume be deducted from the contraction on explosion, the product will represent the contraction due to the combustion of the hydrogen.

Let C = contraction on explosion;

C' = volume of CO_2 produced (i. e., contraction on absorption with KOH).

Then, $C - 2C'$ = contraction due to the hydrogen,

and $\frac{2}{3}(C - 2C')$ = volume of hydrogen.

Again, since the volume of carbon dioxide produced is the same as the volume of marsh gas burned,

$$C' = \text{volume of marsh gas.}$$

The following will make this perfectly clear: A portion of the mixture of hydrogen, marsh gas, and nitrogen employed in the previous example (being the residual gas after the removal of the absorbable constituents from a sample of

coal gas) was measured in the burette, and an excess of air added.

$$\begin{aligned}
&\text{Volume of gas taken} &&= 14.2 \text{ c. c.}\\
&\text{Volume of gas} + \text{air} &&= 97.6 \text{ c. c.}\\
&\text{Volume after explosion} &&= 74.2 \text{ c. c.}\\
\text{Therefore, contraction } &C = 97.6 - 74.2 &&= 23.4 \text{ c. c.}\\
\text{After absorption by } KOH, &\quad \text{volume} &&= 68.2 \text{ c. c.}\\
\text{Therefore, } &C' = 74.2 - 68.2 &&= 6.0 \text{ c. c.}
\end{aligned}$$

Hence, volume of H in 14.2 c. c. of the gas

$$= \tfrac{2}{3}(23.4 - 12) = 7.6 \text{ c.c.},$$

and volume of CH_4 in 14.2 c. c. of the gas $= 6.0$ c.c.,

and volume of N in 14.2 c. c. of the gas

$$= 14.2 - (7.6 + 6.0) = 0.6 \text{ c. c.}$$

Calculating the percentage as in the previous instance,

$$\frac{7.6 \times 86.6}{14.2} = 46.3\% \text{ of hydrogen.}$$

$$\frac{6 \times 86.6}{14.2} = 36.5\% \text{ of marsh gas.}$$

$$\frac{.6 \times 86.6}{14.2} = 3.6\% \text{ of nitrogen.}$$

In cases where the gas under analysis contains a relatively large proportion of nitrogen, as, for example, in the case of producer gas or blast-furnace gases, the addition of air would dilute the gas to such an extent as to render it non-combustible. Under these circumstances, therefore, either oxygen must be substituted for air, or else, after sufficient air has been added to furnish the requisite amount of oxygen, a few cubic centimeters of electrolytic gas may be added to the mixture. The electrolytic gas for this purpose may be generated in the pipette described in Art. **41,** and then transferred to the mercury-explosion pipette.

THE NITROMETER.

50. Many simple processes of gas estimations (such as are necessary when it is only desired to determine one gas by absorption) are conveniently and quickly performed by means of a **nitrometer**, generally called, after its inventor,

Lunge's nitrometer. The apparatus resembles an ordinary gas burette, and consists of a calibrated measuring tube *a*, Fig. 17, connected by means of a piece of rubber tubing to the level tube *b*. By means of the two-way stop-cock on the measuring tube, communication can be established with either the bent capillary tube *d* or the reservoir *c*. Mercury is, as a rule, employed as the confining liquid.

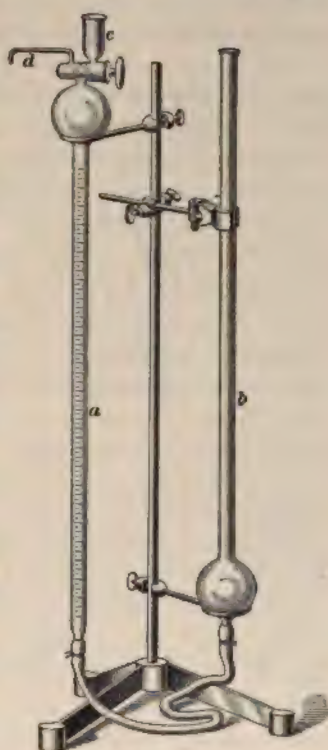


FIG. 17.

To introduce the gas under examination, the level tube is raised until the measuring tube is completely filled with mercury. The capillary *d* is connected to the supply of the gas, and the two-way stop-cock turned so as to open communication between the measuring tube and the capillary, as shown in Fig. 17, and the gas drawn over by lowering the level tube. By turning the stop-cock one-quarter of a revolution, communication with both the exits is cut off.

The absorbing reagent is poured into the reservoir *c* and introduced into the measuring tube by first slightly lowering the level tube and then carefully turning the stop-cock in such a position as to establish a connection between *a* and *c*.

Besides simple absorption operations, this apparatus is particularly adapted for the estimation of the volume of gas that is evolved in certain definite chemical reactions. These processes are sometimes spoken of as *gas-volumetric analysis.* The following are typical examples:

1. The estimation of nitrates, either in commercial niter

or in other nitrates, or in the residue obtained on evaporating water for the determination of nitrates and nitrites.

This process depends on the fact that when a nitrate is decomposed by strong sulphuric acid, in the presence of mercury, this metal is acted on by the liberated nitric acid with the evolution of nitric oxide. The nitric oxide is therefore the measure of the nitric acid or nitrate present. At standard temperature and pressure, 1 cubic centimeter of NO gas weighs .001343 milligrams, and represents .002417 N_2O_5, .004521 KNO_3, and .003805 $NaNO_3$.

For the analysis, the equivalent of about .2 gram of nitrate should be used for each test, dissolved in as little water as may be found convenient. With fairly pure nitrates, a solution of 10 grams of the sample in 250 cubic centimeters of water (of which 2 to 3 cubic centimeters are used for a test) would be a good proportion. This is likely to afford something less than 30 cubic centimeters of gas. The manipulation is very simple: 2 or 3 cubic centimeters of the nitrate solution are poured into the reservoir *c* and are carefully drawn into the measuring tube (previously filled with mercury), and the reservoir rinsed with 1 cubic centimeter of distilled water, which is allowed to pass into the tube. A little practice will enable the operator to perform this without admitting any air, but, should air be drawn in, it may be expelled by raising the level tube slightly, and cautiously opening the tap. The reservoir is again rinsed by the introduction of about 5 cubic centimeters of strong sulphuric acid, the level tube is lowered, and, after that, the stop-cock cautiously opened to admit the sulphuric acid to the measuring tube, the stop-cock being closed before the last few drops of acid run out of it. This is repeated twice with about 3 cubic centimeters of sulphuric acid each time. As soon as the sulphuric acid mingles with the nitrate solution, the reaction begins, and gas is generated as well as heat, so that it will require a more decided lowering of the level tube to draw in the last portions of sulphuric acid.

After the charge and rinsings are all in, the tube should be tipped over to a position nearly horizontal and then back

to the vertical, in order to thoroughly mix the solutions. Raising and lowering the graduated tube will also assist the mixing. The apparatus is then set aside for the reaction to become complete and in order that the gas may take the temperature of the room. Before reading the volume of gas, in order to compensate for the column of acid in the measuring tube, a similar volume of acid of the same dilution is poured into the level tube.

2. By means of a short rubber tube, the capillary *d* may be attached to a small flask fitted with a rubber stopper carrying a short glass tube. If, in the flask, a chemical reaction resulting in the evolution of gas at the ordinary temperature is carried out, the volume of the evolved gas can be measured. With such an arrangement, the estimation of carbon dioxide in carbonates may be made. The direct estimation of manganese dioxide may be made by measuring the carbon dioxide evolved by the action of the manganese dioxide on oxalic acid in presence of sulphuric acid, according to the equation:

$$MnO_2 + H_2SO_4 + C_2H_2O_4 = MnSO_4 + 2H_2O + 2CO_2$$

Similarly, by the action of hydrogen peroxide on manganese dioxide, potassium permanganate, and bleaching powder, the oxygen evolved is a measure of the available oxygen in these compounds, half the oxygen given off in each case being derived from the compound, while the other half is from the hydrogen peroxide, as is seen from the following equations:

$$MnO_2 + H_2O_2 = MnO + H_2O + O_2{}^*$$

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2$$
$$= K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

$$CaCl(OCl) + H_2O_2 = CaCl_2 + H_2O + O_2$$

A weighed quantity of the substance to be tested is introduced into the flask. In the case of manganese dioxide or potassium permanganate, dilute sulphuric acid is added; but, with bleaching powder, a small quantity of water only

*In the presence of sulphuric acid.

is added. The reagent, which in the three above mentioned cases is hydrogen peroxide, is placed in a test tube, and deposited within the flask without allowing any of it to come in contact with the materials already present. The rubber stopper is inserted into the mouth of the flask and the apparatus connected to the nitrometer.

To insure that the air within is under atmospheric pressure, the two-way stop-cock is turned so as to open communication between the flask and the measuring tube, and the level tube adjusted so that the mercury stands at the same level in both tubes. The stop-cock is then turned so as to connect the reservoir *c* with the measuring tube, and the air from the latter entirely expelled, and the tube is filled with mercury by raising the pressure tube. The stop-cock is then closed and the level tube slightly lowered. Communication with the flask is again established and the contents of the little tube tipped out into the flask so as to produce the desired reaction. As the gas is evolved, the level tube is gradually lowered in order to avoid the creation of any unnecessary pressure in the apparatus. When the action is completed, the mercury is brought to the same level, and the apparatus allowed to stand for about half an hour for the gas to regain the atmospheric temperature, when the volume is read off. The atmospheric temperature and pressure are noted and the usual corrections made.

ANALYSIS OF CHIMNEY GASES.

51. The analysis of chimney gases is a frequent occurrence in factories and works of all kinds, the percentage (by volume) of oxygen, carbon dioxide, carbon monoxide, and nitrogen being, as a rule, required. The determination of these gases has been already described in the preceding articles, but as especially constructed apparatus are mostly used for this purpose, those which, owing to their convenient form, compactness, and simplicity of manipulating, are most frequently met, will be briefly described in the following articles.

52. **Modified Elliott Apparatus.**—The modified Elliott paratus shown in Fig. 18 consists of two glass tubes: which has a capacity of about 120 to 130 cubic centi-

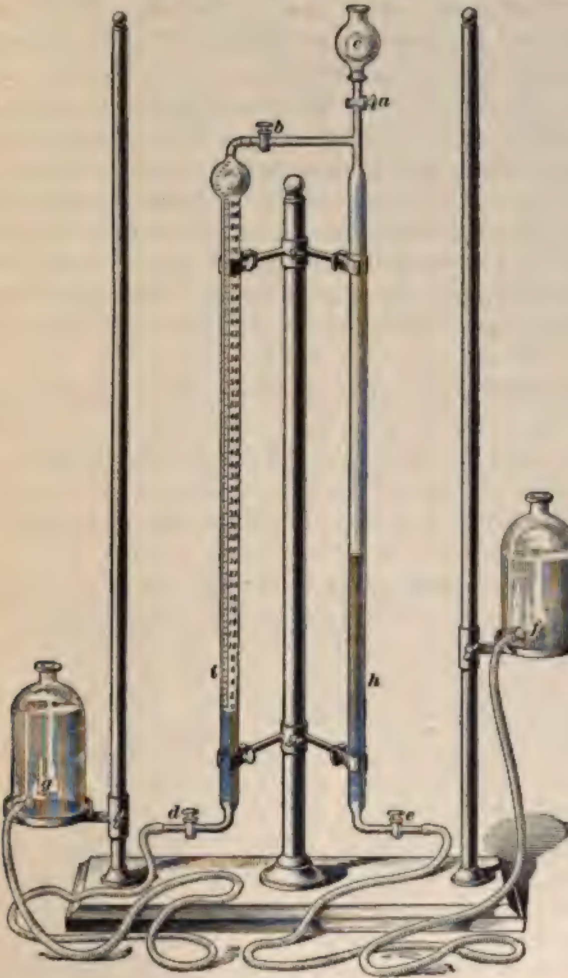


FIG. 18.

ters and which is accurately graduated from 0 to 100 bic centimeters in one-tenth cubic centimeters, and the graduated tube *a h*. At *d* and at *e*, a three-way glass

stop-cock connects each of these tubes with a water-supply bottle. The bottles are shown at *g* and *f*.

53. Manipulation of the Apparatus.—The manipulation of the apparatus is as follows: The funnel cap *c* is removed and in its place is connected a glass tube of small diameter; this tube must be of sufficient length to reach well into the flue from which the gas to be analyzed is taken. The stop-cocks *a* and *b* are opened, and the water-supply bottles *f* and *g* are slowly raised until both tubes as well as the glass tube that leads into the flue are filled with water, care being taken that no air remains in the tubes, and that the displacement of water is complete. The bottle *f* is now gradually lowered, which causes the tube *a h* to be filled with gas.

As soon as sufficient gas has been obtained for the analysis, the lower portion of the tube containing water 2 or 3 inches above the point *h*, the stop-cock *a* is closed, the small glass tube reaching into the flue disconnected, and the cap *c* replaced. After the gas is allowed to remain in the tube *a h* for about 15 minutes, to adjust its temperature to that of the room, and thus insuring accurate measurement, the bottle *g* is slowly lowered until the surface of water therein is on an exact level with zero mark on the tube *i b*; the stop-cock *b* is then opened and the bottle *f* gradually raised until a sufficient quantity of gas has been transferred from *h a* to *i b*, which will be indicated by the volume taken, reading from the mark *0* on the graduated tube *i b* to the mark *100* immediately in contact with the stop-cock *b*.

Having thus obtained 100 cubic centimeters of the gas, the stop-cock *b* is closed and *f* is raised until all the remaining gas in *a h* and *a b* is displaced by the water. The first constituent of the gas to be determined is carbon dioxide. The gas is transferred to the tube *a h* by raising *g* and opening *b*, keeping *a* closed and *f* lowered. When the water reaches *b*, the latter is closed. In the funnel cap *c* are placed 50 cubic centimeters of caustic potash. This solution is made by dissolving 280 grams of potassium hydrate in 1,000 cubic

centimeters of distilled water. The stop-cock *a* is partially opened, so that the potassium-hydrate solution in *c* may slowly drop down through the gas in the tube *a* and absorb the carbon dioxide in doing so.

When all but 2 or 3 cubic centimeters of the potassium-hydrate solution has passed through *a*, the latter is closed, thus preventing entrance of any air; *b* is opened, *f* is slowly raised, and *g* lowered. The raising of *f* is continued until the water in the tube *h a* reaches the stop-cock *b* and the latter is immediately closed. The gas is allowed to stand in the tube *i b* five minutes before taking the reading of the volume on the tube, bearing in mind that the level of the water in *g* must be on a level with the water in *i b* to obtain equal pressure. The difference between *0* and the point indicated by the water in the tube *i b* will give the amount of carbon dioxide absorbed from the gas by the potassium-hydrate solution.

Thus original volume indicated	=	0.0
After absorption of CO_2	=	12.1
Carbon dioxide	=	12.1, or 12.1% carbon dioxide by volume.

To obtain the oxygen, the gas is transferred from *i b* to *a h*, as described before, and in *c* is placed 50 cubic centimeters of an alkaline solution of pyrogallol. A suitable solution is prepared by dissolving 10 grams of pyrogallol in 25 cubic centimeters of distilled water, placing it in *c*, and adding 35 cubic centimeters of the potassium-hydrate solution. This is allowed to pass slowly through *a* and gradually absorbs the oxygen in the gas; *a* is closed before all the liquid passes out of *c*. The operation is once repeated, and the gas transferred in the usual manner to *i b*, where it is measured after it has been resting there for 5 minutes.

Previous reading	=	12.1
After absorption of O	=	18.5
Oxygen	=	6.4, or 6.4% oxygen by volume.

Before transferring the residual gas to *a h* for the determination of the carbon monoxide, all the water in *f* and *a h*

must be replaced by fresh distilled water; to do this, the three-way cock *e* and *a* are opened, when the water will run out of *c* and may be caught in a beaker; *f* and *a h* are thoroughly washed 2 or 3 times with water; *e* is closed in such a way that connection with *f* is again established; *f* is filled with fresh water and raised, and, when the tube *a h* is filled up to *a*, the latter is closed and *f* lowered; *g* is then raised and *b* opened, thus transferring the gas to *a h* for treatment with a solution of cuprous chloride to determine CO.

A suitable cuprous-chloride solution is prepared by dissolving 30 grams of cuprous chloride in 200 cubic centimeters of hydrochloric acid (Sp. Gr. 1.19) and using 50 cubic centimeters of it, as soon as the solution has approximately obtained the temperature of the room. Experience has shown that a freshly prepared solution is much more effective as an absorbent of CO than one that has been standing for some days. In *c* are placed 50 cubic centimeters of this solution, and it is allowed to slowly drop through *a* and absorb the CO as it passes through the gas. This absorption should be repeated 2 or 3 times. The heat generated during this absorption often causes such an increase in the volume of the gas that, when the latter is transferred to the measuring tube, inaccurate readings are obtained. To insure accuracy, the following should be observed:

The gas, after fifteen minutes, is transferred in the usual way to *b i* and the water in *f* and *a h* is replaced by fresh water. The gas is then returned to *a h* and a solution of potassium hydrate is placed in *c* and allowed to drop through the gas in *a h*, absorbing all traces of hydrochloric gas. This process is once repeated, the gas returned to *b i*, and, after allowing it to stand for 15 minutes, the volume is accurately measured.

Previous reading	=	1 8.5
After absorption of CO	=	2 0.0
Carbon monoxide	=	1.5 or 1.5% carbon monoxide.

The nitrogen present is obtained, as in previous experiments, by difference.

Thus, the analysis will read:

Carbon dioxide	=	12.1
Oxygen	=	6.4
Carbon monoxide	=	1.5
Nitrogen	=	80.0
Total	=	100.0

In this analysis, no corrections are required for the tension of the aqueous vapor, since the original gas is saturated with moisture, and, during the analysis, all measurements are made over water.

54. Orsat-Muenke Apparatus.—In the writer's opinion, the apparatus that is best adapted for the rapid determination of carbon dioxide, oxygen, and carbon monoxide is the *Orsat-Muenke;* it is readily portable, not liable to be broken, easy to manipulate, sufficiently accurate for all technical purposes, and always ready for use.

The apparatus, shown in Fig. 19, consists of the graduated measuring burette *a*, of 100 cubic centimeters capacity; it is jacketed with water, to prevent changes of temperature affecting the gas volume; the first 45 cubic centimeters are usually divided into one-tenth cubic centimeters, while the remaining 55 cubic centimeters are divided into cubic centimeters only. The burette ends in a thick capillary tube, which is fastened at both ends, at *b* in a cut of the dividing panel, and at *c* by means of a small brace attached to the cover of the case. The capillary tube is bent at its further end and connected with the U tube *d* containing some loose cotton, and at the bend is filled with water in order to retain all dust and to saturate the gas thoroughly with moisture before measuring takes place. The rear end of the three-way cock *e* is connected by means of a rubber tube *f* with the rubber aspirator *g*, which fills the tube with the gas to be analyzed. The absorption of the different constituents of the gas under examination takes place in the U-shaped absorption pipettes *h*, *i*, and *j*, which are connected with the stoppers by short rubber tubes. For the enlargement of the

absorbing surfaces, *h*, *i*, and *j* are filled with glass tubes. Since the mark *k* is above the place of connection, the latter is always moistened by the respective liquid, and, therefore,

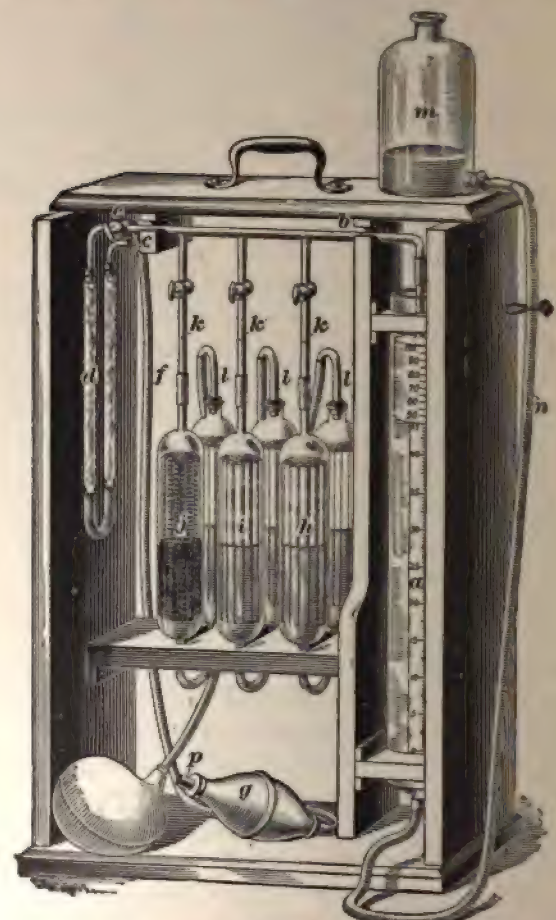


FIG. 19.

can easily be maintained air-tight. The other end of the absorption pipettes is closed by a rubber cork, which contains the small tube *l*; the small tubes are all connected to one rubber bulb of about 200 cubic centimeters capacity, in

order to keep out the atmospheric oxygen. The entire apparatus is enclosed in a wooden case.

55. Charging the Orsat-Muenke Apparatus.—The glass jacket surrounding the burette *a*, as well as the bottle *m*, is filled with distilled water. In order to fill the three absorption pipettes, the stoppers are removed, as well as the glass tubes *l* and the rubber aspirator *g*, and 110 cubic centimeters potassium-hydrate solution, Sp. Gr. 1.26, are poured into the pipette *h*, so that the latter is about half full. This is for the absorption of CO_2. The pipette *i* contains a solution of 18 grams of pyrogallol in hot water, which is poured into it, and then 70 cubic centimeters of potassium-hydrate solution, Sp. Gr. 1.26, are added, whereby the oxygen is absorbed in the gas under examination. The carbon monoxide is absorbed in the pipette *j*, which contains a solution of cuprous chloride made as follows: 35 grams of cuprous chloride are dissolved in 200 cubic centimeters of concentrated hydrochloric acid, 50 grams of copper clippings added, and the mixture allowed to stand in a glass-stoppered bottle for 24 hours.

Each glass tube in *j* contains a spiral of copper wire. To this solution is added 100 cubic centimeters of water, and enough is transferred to *j* to fill it to the required point. The solutions in the rear section of *h*, *i*, and *j* are transferred to the front part of the pipettes, where the absorption of the gases takes place as follows: The three glass stoppers are closed, the stop-cock *e* turned horizontal, and the bottle *m* containing distilled water raised so that the water fills the burette *a*; give a quarter-turn to the left to the stop-cock *e*, so that the second passage leads to the tube *d*, open the stop-cock of the absorption pipette *h*, lower the bottle *m*, and carefully open the pinch cock placed on the tube *n*, so that the potassium-hydrate solution rises to the mark *k*, whereupon the stop-cock is closed.

The reagents of the two other absorption pipettes are raised in an exactly similar way to *k*. The three stoppers with glass tubes *l* are then attached. About 1 cubic centimeter

of water is placed in the tube *d*, loose cotton is placed in both sides, the stopper reinserted and again connected. After filling the burette *a* with water to the 100-cubic-centimeter mark by raising the bottle *m*, the stop-cock is turned so that the connection of the rubber aspirator *g* with the chimney containing the flue gases is brought about through the tube *p*. Aspiration of the gas into the apparatus is now performed by compressing *g* 10 to 15 times, until the whole conductor is filled with gas. This is easily done by compressing *g* with the left hand, closing the attached tube *f* with the thumb of the right hand, and then, on opening the left hand, allowing *g* to expand, raising the thumb again, compressing *g*, etc., until the object is obtained. To fill the burette *a* with the gas, the stop-cock *e* is turned horizontal, the pinch cock of the tube *n* opened, and the bottle *m* lowered until the gas reaches the zero point in *a*, whereupon *e* is closed.

56. Manipulation of the Orsat-Muencke Apparatus. To determine the carbon dioxide, the stop-cock of the absorption pipette *h* is opened and *m* raised with the left hand, so that on opening the pinch cock of *n* with the right the gas enters *h*; *m* is lowered again until the potassium-hydrate solution in *h* reaches to about the tube connection under *k*, and once again drives the gas into the potassium-hydrate vessel by raising *m*. This is repeated 2 or 3 times, and the gas returned to the burette *a* by opening the pinch cock of *n*, raising *m*, and closing the stop-cock of *h*. To measure the amount of absorbed carbon dioxide, the bottle *m* is held next to the burette in such a way that the water stands at the same level in both vessels, the pinch cock of *n* is closed, and the remaining volume of the gas read off. This amount, subtracted from 100 cubic centimeters, gives the amount of CO_2.

The gas is then passed into the pipette *i* in the same manner as in *h*, the oxygen being absorbed by the alkaline pyrogallate solution. This absorption is repeated 3 or 4 times, and the gas returned to the measuring tube, and the

amount of absorption read off. The gas is then passed into the pipette *j* for the absorption of carbon monoxide. After repeating for a number of times the absorption in *j*, the gas is passed into *h* before measurement in *a* of the absorbed carbon monoxide. This is necessary on account of the vapors of hydrochloric acid retained by the gas after contact with the cuprous-chloride solution in hydrochloric acid. After passing the gas into *h* 3 or 4 times, it is then measured as usual in *a*, the residual gas being nitrogen.

ANALYSIS OF URINE.

PRELIMINARY REMARKS.

57. A complete analysis of urine is seldom, if ever, required, and, as in the case of water, only certain constituents are determined. Some of these constituents are never present in normal urine, but occur in the urine of patients suffering from certain diseases; hence, the mere presence of these constituents is sufficient to prove the disease, and a qualitative examination serves this purpose. But even in these cases, the quantities of such constituents are required to indicate the progress of the disease, and, consequently, a quantitative examination is necessary. Other constituents are always present in urine, and, in these cases, qualitative determinations would, of course, be useless. The indications obtained in these cases depend on the quantities of these constituents present, and, consequently, a quantitative examination is required. Certain qualitative determinations are sometimes valuable in examining urine, and, consequently, the subject was partially treated in *Qualitative Analysis*, Part 2. All the determinations given there may be used in examining any sample, and the determinations of color, reaction, and specific gravity, which are always made, need not be repeated at this point.

58. Selecting a Sample.—As the total amount of each constituent passed in 24 hours is what a physician ordinarily wants to know, and as the composition of the urine varies greatly at different times during the day, the selection of the sample for analysis becomes a matter of importance. Ordinarily, the best method of obtaining a sample is to collect the total amount passed during the 24 hours. The volume of this should be carefully noted, the whole thoroughly mixed, and then samples taken for the different determinations. Then, knowing the total amount passed, and the amount taken for the determination of each constituent, the quantity of each constituent passed in 24 hours is readily calculated.

The results obtained in examining a sample passed at one time may be misleading, both because the total amount passed is not taken into account, and because the composition of the urine examined may not represent the composition of the whole. A sample passed at another time during the day might contain only half, or might contain double, the amount of a constituent that is contained in this sample. Then, if the total amount of urine passed is not known, we have nothing from which to calculate the quantity of each constituent passed. The amount of urine passed in 24 hours is frequently given as ranging from 1,200 to 1,500 cubic centimeters, but cases have fallen under the writer's observation in which the total amount passed in 24 hours was rather less than 600 cubic centimeters; while, in others, more than 2 liters were passed during the 24 hours. Results calculated on a basis of 1,200 or 1,500 cubic centimeters, in any of these cases, would obviously have been misleading.

While this method of taking a sample should usually be followed, circumstances frequently demand that it be modified in order to obtain more complete knowledge than would be afforded in this way. For instance, samples of urine passed shortly after a meal are sometimes alkaline; while, at other times, the reaction is acid. To learn this, samples passed at different times during the day would need to be tested separately. Sometimes when urine contains a very small

amount of albumin, a sample passed on rising in the morning will not reveal a trace of this substance, but a sample passed a short time after a meal will give a distinct reaction for this constituent, and the same may be said of minute quantities of sugar. The best plan in such cases is to examine two samples, one passed about an hour after dinner and the other passed on rising in the morning.

Whatever method of collecting a sample is employed, it should be remembered that urine decomposes quite rapidly on standing, especially in a warm place; hence, the sample should be kept in a cool place, and should be examined as soon as possible after it is collected. The chemist's duty ends with the accurate determination of the various constituents, and the interpretation of the results obtained falls within the province of the physician; hence, the pathological significance of the different constituents will not be discussed here.

The principal determination made in the examination of urine are color, reaction, specific gravity, sugar, albumin, urea, uric acid, and chlorides. The total quantity passed in 24 hours should also be noted. As the total amount passed in 24 hours is learned by merely keeping all that is passed and measuring it in a graduated vessel, and as the determinations of color, reaction, and specific gravity have been fully described in *Qualitative Analysis*, Part 2, it is unnecessary to further treat these determinations here, and we will consequently pass on to the description of the others.

SUGAR.

59. A careful qualitative test for sugar should first be made, and if this shows that the urine is free from sugar, the quantitative determination is, of course, omitted. If, however, sugar is found to be present, the next step is to determine its quantity. The quantitative estimation of sugar is accomplished by means of Fehling's solution, but when this is to be used for quantitative determinations, greater care is required in making up the copper solution. Strictly pure

copper-sulphate crystals that have not lost water of crystallization must be used; exactly 34.652 grams of these must be dissolved, and the solution made up to exactly 500 cubic centimeters. Otherwise, the solution is prepared as directed in Art. **78**, *Qualitative Analysis*, Part 2.

60. Determination of Sugar.—When ready to make a determination, thoroughly mix exactly 10 cubic centimeters of the copper-sulphate solution, and an equal amount of the alkaline solution of sodium tartrate. A portion of this solution may be used for the qualitative test. Then measure exactly 2 cubic centimeters of the solution just prepared into a small flask, dilute it to 10 cubic centimeters, and boil it for 15 or 20 seconds, to see that it does not decompose. If it remains clear, add a few drops of a dilute solution of glucose or honey, and again bring the solution to the boiling point, to see if a precipitate forms promptly, thus testing the solution. If the solution decomposes when boiled, or if a red precipitate is not formed when the glucose is added, there is something wrong with the solution, and a new one must be prepared. This will never happen if pure materials are used, and the solution properly made up.

When a solution is obtained that does not decompose on boiling and that gives a precipitate when a few drops of glucose solution are added, rinse out the flask thoroughly, introduce exactly 2 cubic centimeters of the Fehling solution, and dilute it to 10 cubic centimeters with distilled water. Place the flask on a gauze over a burner, and, as soon as the contents commence to boil, remove it, and add a little of the urine under examination from a burette. The amount of urine that it is safe to add at first will be indicated by the qualitative test. Heat the solution just to boiling, remove it from the heat immediately, give it a rotary motion to secure thorough mixing, allow the precipitate to partially settle, and note the depth of the blue color of the solution. Then continue the addition of urine, a little at a time, bringing the solution just to the boiling point after each addition, until the blue color of the solution is just discharged. From

the amount of urine added to just decolorize the solution, calculate the percentage of sugar in the sample.

The calculation is based on the fact that the 2 cubic centimeters of Fehling's solution used are reduced by .01 gram of sugar; hence, the volume of urine required to decolorize the solution contains .01 gram of sugar. As the specific gravity of urine is never very much greater than 1, it is generally assumed in making this calculation that the specific gravity of the sample is 1, or, what is the same thing, that 1 cubic centimeter of it weighs 1 gram. This is never exactly correct, but is sufficiently accurate for practical purposes. Using this as a basis of calculation, if 1 cubic centimeter of the urine is required to discharge the blue color, the sample contains 1 per cent. of sugar; if .5 cubic centimeter is required, the sample contains 2 per cent. of sugar; and if 2 cubic centimeters are required, the solution contains .5 per cent. of sugar. If more accurate results are required, the specific gravity of the urine must be taken into account.

This titration is, in a sense, the reverse of any so far performed, inasmuch as the reagent is measured out, and the sample added; hence, the greater the amount of sample added from the burette, the lower the percentage of sugar indicated. If a sample contains much sugar, it is best to measure exactly 10 cubic centimeters of it into a graduated 100-cubic-centimeter flask, dilute it exactly to the mark with distilled water, and use this diluted sample for the determination. In this case, an appropriate calculation must, of course, be made in reckoning the result.

ALBUMIN.

61. Albumin occurs in the urine of patients suffering from some diseases of the kidneys, and the qualitative methods given in Art. **79**, *Qualitative Analysis*, Part 2, are sufficient to indicate these. But, in many cases, it is important that the physician should know the relative amount of albumin contained in the urine from day to day, and, for this purpose, quantitative methods are required. At present

we have no very satisfactory method for the quantitative determination of albumin. Probably the most accurate one is the gravimetric method, in which the albumin is precipitated by heating the sample and adding an acid; but this method is long and troublesome, and the results obtained by one of the shorter approximate methods are frequently accurate enough for practical purposes. Two methods frequently used are here given.

62. Gravimetric Determination.—Measure 100 cubic centimeters of the sample into a beaker, stand it on a gauze over a burner, and, just as it begins to boil, add 10 or 12 drops of nitric acid of 1.2 Sp. Gr. Mix the solution, cover the beaker with a watch glass, allow it to stand undisturbed for at least 12 hours, and then filter through a paper that has been dried at 100° and weighed. Wash the precipitate and filter thoroughly, dry at 100° until a constant weight is obtained, and, from the weight obtained, calculate the percentage of albumin in the sample.

Acetic acid is frequently used instead of nitric acid to precipitate the albumin, and in some ways it is preferable; but in some cases it forms a slimy precipitate that it is almost impossible to filter. The method is tedious at best, and the following method, which yields approximate results, is usually sufficiently accurate for the purpose of comparison:


FIG. 20.

63. Determination With Esbach's Albuminimeter.—In using **Esbach's albuminimeter,** the albumin is precipitated by an acid mixture and the percentage is indicated approximately by the size of the precipitate. The albuminimeter is simply a graduated tube shown in Fig. 20. To make the determination, fill the tube to the mark *U* with the urine to be tested, then add the Esbach reagent to bring the liquid to the mark *R* when the tube is standing in an upright position. Close the tube with the rubber stopper provided

for the purpose, cautiously mix the contents, and allow the tube to stand, undisturbed, in an upright position for 24 hours. The albumin will be coagulated by the acid reagent, and will settle to the bottom of the tube, so that the amount present may be read off.

In mixing the urine and reagent, place the stopper in the tube and slowly invert it, then bring it back to an upright position, and repeat this 10 or 12 times, but do not shake or agitate the liquid violently. Each graduation line at the bottom of the tube indicates 1 gram of albumin in a liter of urine. For example, if the precipitate of albumin reaches to the second line from the bottom, it indicates that 1 liter of the urine contains 2 grams of albumin, or that the sample contains .2 per cent. of this constituent. Knowing the amount of albumin in a liter, and the total amount of urine passed, the amount of albumin passed in 24 hours is readily calculated.

The urine used for this determination should have an acid reaction, and, as albuminous urines are sometimes neutral or even alkaline, the reaction should always be determined before this estimation is commenced. If the urine is found to be neutral or alkaline, pour approximately the amount needed for the determination into a beaker and add acetic acid, drop by drop, while stirring the sample, until a drop of the urine, removed on the stirring rod and brought in contact with blue litmus paper, imparts a red color to it; but avoid a large excess of the acid. More than 3 drops of the acid will seldom be required. This acidulated sample is used for the determination.

The results obtained by this method are more accurate and concordant when only small quantities of albumin are present. Consequently, when the qualitative test indicates a large amount of albumin, it is best to dilute a portion of the sample with distilled water. The amount of water to be added will depend on the amount of albumin in the urine. It is best to dilute the sample until it contains less than 5 grams per liter of albumin. Of course, an appropriate calculation must be made in obtaining the result, in case the sample is diluted in this way.

Esbach's solution, used to precipitate the albumin, is made by dissolving 10 grams of picric acid and 20 grams of citric acid in distilled water, and diluting the solution to 1 liter. The picric acid is to coagulate the albumin, and the citric acid to hold the phosphates in solution. The solution should be kept in a tightly stoppered bottle. As this method only gives approximate results at best, it should be carefully performed. The solution should always be allowed to stand just 24 hours before taking the reading.

UREA.

64. As **urea** is the most abundant solid constituent of urine, and is always present, a qualitative examination for this constituent is never required, but its quantitative estimation is frequently a matter of importance. Methods based on two different principles are largely employed for its determination. The volumetric method proposed by Liebig was used almost exclusively until recently. This method depends on the fact that mercuric nitrate precipitates urea quantitatively. Recently, it has been largely superseded by a process in which the urea is decomposed by an alkaline solution of hypobromite and the nitrogen evolved measured.

A number of forms of apparatus for carrying out this process have been suggested by different chemists. The forms devised by Hüfner and Doremus are described here. It has been objected to the hypobromite process that the results obtained by it are too low, and this is true if the results are calculated from the theoretical composition of urea; but as the results are usually calculated from the amount of nitrogen found by experiment to be liberated by a given weight of urea, this objection will scarcely hold good. At all events, the results obtained by this process are sufficiently accurate for practical purposes. The older process will be described first.

65. Liebig's Method.—For this method, we need a standard solution of mercuric nitrate of such strength that

1 cubic centimeter is exactly equivalent to .01 gram of urea, a saturated solution of pure sodium carbonate, and a barium solution made by mixing 1 volume of a cold saturated solution of barium nitrate with 2 volumes of a cold saturated solution of barium hydrate. A standard solution of mercuric nitrate, made by dissolving 77.2 grams of pure mercuric oxide in nitric acid and diluting to 1 liter with water, will be of the proper strength for use. It is prepared as follows:

Dissolve 78 grams of mercuric oxide in nitric acid; by the aid of heat, evaporate the solution to a syrupy consistency over a water bath, and dilute this syrupy liquid to somewhat less than 1 liter with distilled water. If a precipitate of basic nitrate separates when the water is added, allow it to settle and decant the clear liquid. Then dissolve the precipitate in the least necessary quantity of nitric acid; add this to the main solution, and mix the whole thoroughly, and standardize it against a urea solution of known strength.

For this purpose, dissolve 2 grams of pure urea in distilled water, dilute it to exactly 100 cubic centimeters, and mix it thoroughly. A solution is thus obtained 10 cubic centimeters of which contain .2 gram of urea. Measure exactly 10 cubic centimeters of this solution into a beaker, and slowly introduce the mercuric nitrate solution from a burette while stirring constantly. As the mercuric nitrate falls into the urea solution, it produces a dense precipitate. When the precipitation seems to be nearly complete, remove a drop of the solution from the beaker on a stirring rod, and bring it in contact with a drop of the saturated solution of sodium carbonate placed on a suitable surface. Some chemists use a *spot plate* or porcelain slab for this purpose, while others prefer a piece of glass standing on a black ground.

If the urea is not completely precipitated, there will be no change of color. Continue to add the mercuric nitrate cautiously, testing after each addition, until a yellow color is produced when a drop of the solution is brought in contact with a drop of the sodium carbonate. This indicates that the urea is completely precipitated, and that the solution

contains a trace of mercuric nitrate, which reacts with the sodium carbonate. Note the reading of the burette, and, from this, calculate how much the solution must be diluted. Add water to the solution until, after thorough mixing, just 20 cubic centimeters of it are required to precipitate the urea in 10 cubic centimeters of the solution and give a faint yellow tinge to a drop of sodium carbonate. The solution will now be of such strength that 1 cubic centimeter of it represents .01 gram of urea.

Having, now, an accurately standardized solution of mercuric nitrate, we are prepared to determine the urea in a sample of urine. This is accomplished as follows: Measure exactly 40 cubic centimeters of the urine into a beaker, add 20 cubic centimeters of the barium solution, and stir thoroughly. The barium solution precipitates the sulphates, carbonates, and phosphates. Filter through a dry filter placed in a dry funnel, and receive the filtrate in a dry, clean beaker. If a good quality of filter paper is used, the filtrate should be clear, but if cloudy, it should be passed through the paper a second time. Measure into a beaker 15 cubic centimeters of the filtrate, which, of course, will contain 10 cubic centimeters of the urine, and add standard mercuric nitrate solution from a burette until a drop of the solution, when brought in contact with a drop of sodium carbonate, produces a yellow color of the same depth as that obtained in standardizing the mercuric nitrate solution.

From the quantity of standard mercuric nitrate used, calculate the percentage of urea in the sample, or the amount passed in 24 hours. With normal urine, the specific gravity serves as a guide in making the titration. A number of cubic centimeters of mercuric nitrate approaching the last two figures of the specific gravity, may usually be added before testing for the end of the reaction. Thus, if the specific gravity of the urine is 1.020, it is generally safe to add 18 cubic centimeters of mercuric nitrate before mixing a drop of the solution with sodium carbonate.

The results obtained by this method are usually correct enough for practical purposes, but their accuracy may be

increased by certain corrections and modifications. Those frequently applied are as follows:

If the urine contains more than 1 per cent. of sodium chloride, 2 cubic centimeters are deducted from the total quantity of mercuric nitrate required to produce the yellow color with sodium carbonate before the calculation is made. It has been found by experiment that about this amount of the mercuric solution is used up by the sodium chloride. If still greater accuracy is required, the chlorine is first determined, just enough silver nitrate is added to precipitate it in the sample used, and the silver chloride is filtered off before the barium solution is added. This is a rather troublesome process, however, and is seldom resorted to.

If the urine contains more than 2 per cent. of urea, that is, if more than 20 cubic centimeters of mercuric nitrate are required for its precipitation, a second sample must be titrated after adding to it half as much water as there was mercuric nitrate required in excess of 20 cubic centimeters in the first titration. For instance, if 26 cubic centimeters of mercuric nitrate are added to the first sample, this would be 6 cubic centimeters in excess of 20, and, consequently, 3 cubic centimeters of water must be added to the second sample before titrating it.

If the urine contains less than 2 per cent. of urea, .1 cubic centimeter is subtracted from the total for each 4 cubic centimeters less than 20 of the mercuric nitrate solution used. Thus, if 12 cubic centimeters of mercuric nitrate are required, 8 cubic centimeters less than 20 are used, and, consequently, .2 cubic centimeter must be deducted; hence, 11.8 cubic centimeters of mercuric nitrate should be taken in making the calculation.

If much albumin is present, it interferes with the titration, and should, consequently, be removed. This is done as follows: Measure out exactly 50 cubic centimeters of the urine, add 2 drops of strong acetic acid, and boil the solution a few moments to coagulate the albumin. After allowing the precipitate to completely settle, decant exactly 30 cubic centimeters of the clear solution, add 15 cubic centimeters

of the barium solution, filter off the precipitate, and proceed with the determination as usual. If the precipitated albumin remains at the bottom of the vessel, 40 cubic centimeters of the clear liquid may be decanted and mixed with 20 cubic centimeters of the barium mixture.

66. Determination With Hüfner's Apparatus.—For this determination, we need an alkaline solution of sodium hypobromite. It is made by dissolving 100 grams of sodium hydrate in 250 cubic centimeters of distilled water, and slowly stirring in 25 cubic centimeters of bromine, when sodium hypobromite is formed according to the equation:

$$2NaOH + Br_2 = NaBr + H_2O + NaBrO$$

Hüfner's apparatus is shown in Fig. 21. The lower bulb a, which is fitted into a wooden support, is connected with the bulb c by means of a tube containing the stop-cock b. The upper part of the bulb c is drawn out to a tube, the exterior of which is of ground glass. The perforated glass vessel d fits over this tightly, and the graduated tube e fits over it loosely inside of the vessel d.

FIG. 21.

To determine the urea by means of this apparatus, measure accurately about 2 cubic centimeters of the urine into the bulb a, and fill this to the top of the stop-cock with freshly distilled water. Close the connection between the two bulbs by turning the stop-cock, and fill the bulb c with equal parts of hypobromite solution and freshly distilled water. Fit the vessel d over the tube of the bulb c, making sure that the connection is tight, and pour in enough distilled water to cover the end of the tube. Then fill the graduated reading tube with distilled water, and invert it over the tube at the top of the bulb c, as shown in the figure. Be sure that the apparatus contains no air bubbles. Now

turn the stop-cock b, and allow the hypobromite and urine to mix. The hypobromite immediately attacks the urea, liberating carbon dioxide and nitrogen according to the equation :

$$CO(NH_2)_2 + 3NaBrO = 3NaBr + 2H_2O + CO_2 + N_2$$

The carbon dioxide is absorbed by the excess of sodium hydrate in the hypobromite solution, and the nitrogen collects in the reading tube c. When the reaction is complete, and the gas has all collected in the reading tube, transfer this to a vessel of water that has been standing in the room for some time, to acquire its temperature, taking care not to allow any air to enter the tube. After suspending it in this water for a few minutes, bring the level of the water in the tube to the level of that on the outside, and carefully note the volume of nitrogen when the pressure is thus equalized. Then immediately note the temperature and barometric pressure. The urea is then calculated by the formula:

$$W = \frac{100\,v\,(P-p)}{760 \times 354.33\,a\,(1+.00366\,t)}; \qquad (5.)$$

in which

W = weight, in grams, of urea in 100 cubic centimeters of the urine;
a = volume of urine taken;
v = volume of nitrogen obtained, in cubic centimeters;
t = observed temperature, in centigrade degrees;
P = observed barometric pressure, in millimeters;
p = tension of aqueous vapor for the temperature t.

Having now the weight of urea in 100 cubic centimeters of the urine, the amount passed in 24 hours, or the percentage, is readily calculated. In calculating the percentage of urea, the weight of 100 cubic centimeters of urine is of course obtained from the specific gravity of the sample. In handling the reading tube containing the nitrogen, care should be exercised to avoid touching it with the hands more than is necessary, as the warmth of the hand is sufficient to expand the gas and thus cause an error.

It has been found that when the vessel d contains water.

the water passing out of the reading tube sometimes carries nitrogen with it, and this is allowed to escape. To avoid this loss, a solution of salt is frequently placed in *d*, instead of water.

67. Estimation With Doremus's Apparatus.—For the determination of urea with the Doremus apparatus, pure bromine and a solution of sodium hydrate are required. The sodium-hydrate solution is made by dissolving 100 grams of the solid in 250 cubic centimeters of water. The apparatus is shown in Fig. 22. It consists of a bulb and tube, and a small, curved, nipple-capped pipette, graduated to measure 1 cubic centimeter. The tube of the apparatus is so graduated that each of the small divisions represents .001 gram of urea. On the side of the tube opposite the graduation, two parallel lines are drawn close to each other. To use this ureameter, pour in enough of the sodium hydrate to fill the graduated tube to the parallel lines, then, by means of the nipple pipette, add 1 cubic centimeter of bromine, and when this has completely dissolved, add water to fill the graduated tube and bend up to the bulb.

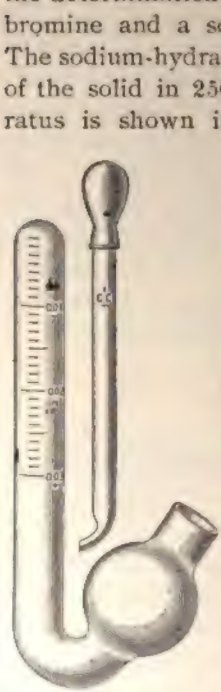


FIG. 22.

Mix the solution in the apparatus, and wash the pipette thoroughly. Draw up exactly 1 cubic centimeter of the urine in the pipette, pass the curved end of it through the bulb of the ureameter as far as it will go in the bend, and, by pressing gently and steadily on the nipple, force the urine out into the graduated tube, which is held in a perpendicular position. As soon as all the urine is expelled, withdraw the pipette, taking care not to press the nipple sufficiently to force air out after the urine. When the urine comes in contact with the hypobromite solution, the urea is decomposed the same as in the Hüfner apparatus.

the carbon dioxide is absorbed by the excess of sodium hydrate, and the nitrogen is collected in the tube, which is so graduated that the nitrogen evolved from 1 milligram of urea just fills one division. After the froth has subsided, read off the number of milligrams of urea contained in the 1 cubic centimeter of urine, and, from this, calculate the percentage or the amount passed in 24 hours.

If preferred, this instrument may be obtained so graduated that each division of the tube represents 1 grain of urea in a fluid ounce of urine. When an instrument thus graduated is used, the weight in grains of urea passed in 24 hours is obtained by multiplying the number of grains indicated by the number of ounces of urine voided. If a number of determinations are to be made, it is handier to make up a quantity of hypobromite solution at once. The solution described for use in the Hüfner apparatus may be mixed with an equal volume of water, and this solution used to fill the tube and bend without further dilution. If only one or two determinations are to be made, however, it is best to prepare the solution in the apparatus, for it must be freshly prepared for use.

This instrument was designed for rapid approximate estimations, but, as it is graduated by experiment at 65° F., the results obtained at this temperature are sufficiently accurate for all practical purposes. In fact, if care is exercised in making the determinations, the results obtained by this method appear to be as accurate as those obtained by other methods, and, on account of its simplicity and the rapidity with which it yields results, this method is very largely used at the present time.

URIC ACID.

68. As **uric acid** is quite insoluble, it never occurs in the free state in normal urine, except, possibly, in minute quantities, and, when it is spoken of as a constituent of normal urine, the acid in combination with metals is meant. It occurs in urine combined principally with sodium, potassium, and ammonium, but also with calcium and magnesium. In

health, it is found in quantities ranging from .4 to .8 gram in 24 hours, and usually varies with the urea, of which it is one stage short in oxidation.

Several volumetric methods for the estimation of uric acid have been proposed, but they are all long and cumbersome, and apparently liable to error; hence, the *gravimetric method* is usually employed.

69. Gravimetric Determination of Uric Acid.—Measure 200 cubic centimeters of the sample into a beaker, add 20 cubic centimeters of hydrochloric acid, mix thoroughly, cover the beaker with a watch glass, and stand it in a cool place for 30 hours. During this time, the uric acid will separate, and will be found in crystals at the bottom of the beaker, and on the sides, adhering to the glass. Filter on a paper that has been dried at a temperature ranging from 100° to 105° and weighed, removing the last of the crystals from the beaker by means of a "policeman." Wash thoroughly with distilled water, and note the volume of the filtrate and washings. Place the filter containing the precipitate in an air bath, and heat it at a temperature ranging from 100° to 105° until a constant weight is obtained. It should be dried for 1 hour at this temperature before making the first weighing. To the weight of uric acid thus obtained, add .0038 gram for each 100 cubic centimeters of filtrate and washings, and, from the weight thus obtained, calculate the percentage of uric acid, or the amount passed in 24 hours.

Neubauer finds that 100 cubic centimeters of the filtrate and washings retain .0038 gram of uric acid, and, consequently, advises the addition of this weight for each 100 cubic centimeters of solution in the filtrate, as directed above.

CHLORIDES.

70. Chlorine exists in urine chiefly in the form of sodium chloride, but also, in smaller quantities, combined with potassium and ammonium. As most of the chlorine is combined with sodium, it has become customary to calculate it

all to sodium chloride, and report it as such. There are a number of methods for the determination of chlorine in urine, but the one that appears to be the most satisfactory and is most largely employed is the volumetric method devised by Mohr. The details of this process are as follows:

71. Mohr's Method.—Measure 10 cubic centimeters of the sample into a platinum crucible, dissolve from 1 to 2 grams of pure potassium nitrate in it, and slowly evaporate to dryness. Then gradually increase the temperature until the organic matter in the residue is completely burned and a white mass remains, but avoid sudden or long-continued heating, lest chlorine be expelled. Dissolve this saline mass in a little distilled water, wash the crucible with a jet of water from a wash bottle, and allow the washings to run into the beaker with the main solution. When the solution is cool, add dilute nitric acid drop by drop until it has a faint acid reaction, and then add a little pure calcium carbonate to neutralize the excess of acid. Filter off the excess of calcium carbonate and wash the chlorides out of the filter with distilled water. To the filtrate, add a few drops of a cold saturated solution of potassium chromate, and then introduce a standard solution of silver nitrate from a burette, while stirring the solution constantly, until a permanent red color is imparted to it. From the amount of silver solution used to precipitate the chlorine, calculate the weight of sodium chloride in 10 cubic centimeters of the urine, and, from this result, calculate the percentage of sodium chloride, or the amount passed in 24 hours.

A standard solution of silver nitrate of almost any strength may be used for this determination, but, if many determinations are to be made, it is handy to have a solution of such strength that 1 cubic centimeter of it represents .01 gram of sodium chloride. This solution may be prepared by dissolving 29.06 grams of pure silver nitrate in distilled water and diluting the solution to 1 liter, but it is better to standardize it against a solution of sodium chloride. If this is done, dissolve the silver nitrate and dilute the solution to a little less

than 1 liter. Then make up a solution of sodium chloride by dissolving 10 grams of the pure solid in distilled water and diluting to exactly 1 liter; 1 cubic centimeter of this solution contains .01 gram of sodium chloride. Measure about 20 cubic centimeters of this solution into a beaker from a burette, dilute it to about 50 cubic centimeters, add a few drops of potassium chromate, and then introduce the silver solution from a burette until a permanent red color is imparted to the solution. From the result thus obtained, calculate how much water must be added to the silver solution, and dilute it until the solutions are exactly matched. The silver nitrate will then be of such strength that 1 cubic centimeter represents .01 gram of sodium chloride.

ANALYSIS OF DAIRY PRODUCTS.

NATURE AND COMPOSITION OF MILK.

72. Milk consists of *water*, *fat*, *proteids*, *sugar*, and *mineral matters*. It is the nutritive secretion of nursing mammals, its secretion being the result of pregnancy and delivery at term, and continues for a variable period. The chemistry of its formation is not entirely understood, and as the organic ingredients of the milk do not exist in appreciable quantities in the blood, they must, therefore, be produced by a specific secretory action.

73. Fat.—*Fat* occurs in milk in globules varying in size from .0015 millimeter to .005 millimeter in diameter; it consists of a mixture of the ethers of tritenyl C_3H_5, but is peculiar among other animal fats in containing a notable proportion of acid radicals with a small number of carbon atoms. Thus, about 91 per cent. consists of stearin, palmitin, and olein, and the remaining 9 per cent. of butyrin and caproin, along with minute amounts of caprin, myristin, and caprylin. The exact arrangement of the constituents is not known, but the

general opinion is that milk fat is not a mixture of simple fats, but that several acid radicals are united to the same tritenyl molecule.

74. Proteids.—It is generally accepted that the proteids in milk exist in at least three forms, *casein*, *albumin*, and *globulin*, the casein being present in by far the greater amount, and the globulin as traces only.

Casein is in a large part, at least, in a gelatinous form, probably in combination with calcium phosphate. It is precipitated from this condition by acids, rennet, magnesium sulphate, and other substances. Acids precipitate the casein by breaking up its combination with calcium phosphate. The action of rennet appears to be a more complex one, and is supposed to depend on the presence of calcium salts; thus, if the curd precipitated by dilute acids is dissolved in a dilute alkali solution and neutralized, it is unaffected by rennet, but regains its coagulability by the addition of a solution of a calcium salt, or, what amounts to the same thing, a little of the whey from which the casein was precipitated. It appears that rennet decomposes the casein into two proteids, one of which is precipitated in the curd. Some chemists use the term "caseinogen" to designate the form in which the casein exists when in solution or precipitated by acids, and reserve the term "casein" for the curd produced by rennet.

The *albumin* of milk appears to be a distinct form, and is generally known as *lactalbumin*. It is not precipitated by dilute acids, but is coagulated by heating to 70° to 75°. The proportion in cow's milk ranges from .35 to .50 per cent., although colostrum (see Art. **76**) may contain a much larger proportion. The composition of lactalbumin is usually given as:

Carbon	52.19%
Hydrogen	7.18%
Nitrogen	15.77%
Oxygen	23.13%
Sulphur	1.73%

Globulin occurs only in minute quantities in normal milk,

but colostrum may contain as much as 8 per cent. It coagulates on heating.

75. Lactose.—This is the sugar of milk and is peculiar to it; it has the composition $C_{12}H_{22}O_{11}$ and crystallizes with 1 molecule of water. In contact with yeast, lactose undergoes alcoholic fermentation, although with difficulty; it undergoes the lactic fermentation, however, very readily under the influence of certain microbes. When milk is evaporated rapidly to dryness, as in the determination of the total solid residue, the milk sugar is left in the anhydrous state.

76. Colostrum.—The term **colostrum** is applied to the milk secreted in the early stage of lactation. Usually, it has a marked difference from ordinary milk. It contains characteristic structures known as *colostrum corpuscles*. They are present for a variable period—3 to 14 days, but may persist even longer. Colostrum usually contains much less fat than fully developed milk, but a larger proportion of proteids, the increase being principally in the albumin and in the globulin. Colostrum is usually acid to litmus.

77. Normal milk is an opaque, white, or yellowish-white, fluid, nearly odorless, with a faintly sweet taste. Its opacity is due partly to the fat globules, although their removal does not render the milk transparent. The reaction of freshly drawn milk is amphoteric, that is, it turns blue litmus paper red, and red litmus paper blue. Its specific gravity varies between 1.028 and 1.035. It undergoes a gradual augmentation for a considerable time, but after about 5 hours, its specific gravity becomes stationary if kept at a temperature of 15°, although, at a higher temperature, it may require 24 hours to acquire constancy. This change is not dependent on the escape of gas, and is believed to be due to some molecular modification of the casein.

Unless collected with special care and under conditions of extreme cleanliness, milk always contains bacteria and animal

matter of an offensive character, such as blood, pus cells, etc. Many minute organisms, especially bacteria, propagate with great rapidity in milk and produce changes in its composition. Some specific organisms, such as the *Spirillum choleræ*, multiply to only a limited extent in ordinary milk, being hampered by other bacteria present, but, when introduced into sterilized milk, increase with great rapidity.

At ordinary temperature, milk soon undergoes decomposition under the influence of the microbes present, by which the milk sugar is converted principally into lactic acid, and the proteids are partly decomposed and partly coagulated. The liquid becomes sour and the fat is enclosed in a coagulated cream. In the initial state of decomposition, the proteids frequently undergo transformation into substances that are the cause of the violent poisonous effects occasionally produced by ice cream and other articles of food into the preparation of which milk enters.

ANALYTICAL PROCESSES.

78. The determinations usually made are those of specific gravity, total solids, ash, fat, total proteids, casein, albumin, and sugar, to which the determinations of the amount of cream and opacity, which give some idea of the quality of the milk, may be added.

ARBITRARY METHODS.

79. Opacity of Milk.—The opacity of the milk is doubtless due to the presence of the suspended fat particles and to the colloid casein. On the latter, it is probably principally dependent, since the color of the milk is not sensibly changed when practically all the fat is removed, as has been previously stated. Some idea of the quality of the milk, however, may be obtained by determining its opacity. This is accomplished by the use of a lactoscope. The one generally employed was devised by Feser, and is shown in Fig. 23.

This instrument consists of a cylindrical glass vessel of little more than 100 cubic centimeters capacity, in the lower part of which is set a cone of white glass marked with black lines. In this part are placed 4 cubic centimeters of milk. A small quantity of water is added and the contents of the vessel shaken. The addition of water is repeated until the black lines on the white glass just become visible. The graduations on the left side show the volume of water that has been added to bring the dark lines into view, while those on the right indicate, approximately, the percentage of fat present.

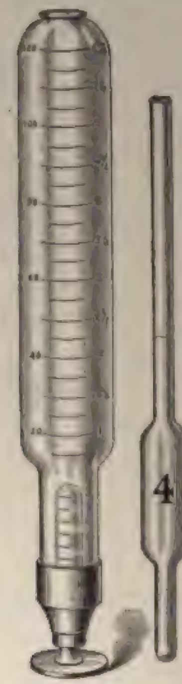


FIG. 23.

80. Creamometer.—The volume of cream that a sample of milk affords under arbitrary conditions of time and temperature is sometimes of value in judging the quality of milk. A convenient creamometer is a small cylinder graduated in such a way that the volume of cream separated in a given time can be easily noted. There are many kinds of apparatus used for this purpose, a typical one being shown in Fig. 24. The usual time for setting is 24 hours.

FIG. 24.

SPECIFIC GRAVITY.

81. The specific-gravity determination is to be made only after the spontaneous rise that is peculiar to milk has ceased. This will require about 5 hours after the milk is drawn, if it has been kept below 15°, but, at a

higher temperature, it will be necessary to allow at least 12 hours. The specific gravity of milk varies in general from 1.028 to 1.034. Nearly all good cow's milk will show a specific gravity varying from 1.030 to 1.032. In extreme cases from single cows, the limits may exceed those first given above, but such milk cannot be regarded as normal.

Increasing quantities of solids, not fat in solution, tends to increase the specific gravity, while an excess of fat tends to decrease it. There is a general ratio existing between the solids not fat and the fat in cow's milk, which may be expressed as 9 : 4. The removal of cream and the addition of water in such a manner as not to affect the specific gravity of the sample, disturbs this ratio. The determination of the specific gravity alone, therefore, cannot be relied on as an index of the purity of milk.

82. Lactometer.—A hydrometer especially constructed for use in the determination of the specific gravity of milk is called a **lactometer.** One of the most commonly used is known as the *lactometer of the New York Board of Health.* It is a hydrometer, delicately constructed, with a large cylindrical air space and a stem carrying the thermometric and lactometric scale, as is shown in Fig. 25. The milk is brought to a temperature of 15.5° and the reading of the lactometer scale observed. This is converted into a number expressing the specific gravity by means of a table of corresponding values accompanying each instrument and given in Table 2. Each mark on the scale of the instrument corresponds to 2 degrees, and these marks extend from 0° to 120°.

The minimum density for whole milk at 15½° is fixed by this instrument at 100°, corresponding to a specific gravity of 1.029. The mean density of many thousand samples of pure milk, as observed by the New York health authorities, is 1.0319.

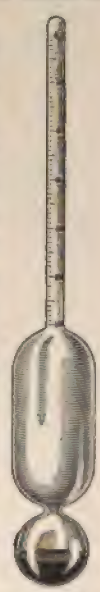


FIG. 25.

TABLE 2.

TABLE SHOWING SPECIFIC GRAVITIES CORRESPONDING TO DEGREES OF THE NEW YORK BOARD OF HEALTH LACTOMETER. TEMPERATURE, 15.5° (60° F.).

Degrees.	Specific Gravity.	Degrees.	Specific Gravity.	Degrees.	Specific Gravity.
90	1.02619	101	1.02928	112	1.03248
91	1.02639	102	1.02958	113	1.03277
92	1.02668	103	1.02987	114	1.03306
93	1.02697	104	1.03016	115	1.03335
94	1.02726	105	1.03045	116	1.03364
95	1.02755	106	1.03074	117	1.03393
96	1.02784	107	1.03103	118	1.03422
97	1.02813	108	1.03132	119	1.03451
98	1.02842	109	1.03161	120	1.03480
99	1.02871	110	1.03190		
100	1.02900	111	1.03219		

TOTAL SOLIDS.

83. The determination of the **total solids** meets with a number of difficulties, and many processes have been proposed. It is not possible here to describe all of them, but two of the most frequently used methods are here given.

84. The determination of total solids is made by evaporating, in a shallow flat dish of platinum from 7 to 8 centimeters in diameter, an accurately weighed quantity of milk. The milk must be spread evenly in a thin layer, and should only cover the dish with a very thin film of milk. If the ash is also to be determined, about 5 grams should be accurately weighed in the dish, evaporated quickly to apparent dryness over the water bath, and the heating continued in the air bath until the weight becomes practically constant, which will require about 3 hours. If the evaporation is

carried on slowly, some decomposition occurs and the residue is brown, but if the larger portion of the water is evaporated quickly, a white residue is obtained. When the ash is not to be determined, it is recommended to use only 1 to 2 grams.

85. Babcock's Method.—When a higher degree of accuracy is required, the method of Babcock, which is adopted by the Association of Official Agricultural Chemists, should be employed. The method is conveniently carried on as follows: Provide a hollow cylinder of perforated sheet metal about 60 millimeters long and 20 millimeters in diameter, closed 5 millimeters from the bottom by a disk of the same material. The perforations should be about .7 millimeter in diameter, and as close together as possible. Fill loosely with from 1½ to 2½ grams of dry woolly asbestos and weigh. Introduce a weighed quantity of milk (about 5 grams). Dry at 100° for 4 hours. During the first part of the drying, the door of the oven should be partly left open to allow the escape of moisture. Cool in a desiccator and weigh; repeat drying until constant weight is obtained. The residue may be preserved for the determination of the fat.

86. Calculations of Total Solids.—As the density of a milk and the amount of fat in it can be quickly and accurately determined, many chemists prefer to calculate the total solids. Many arbitrary formulas have been proposed, and all of them may be used with satisfactory results, when the samples do not vary widely from the normal. A formula giving very satisfactory results, which vary less than .05 per cent. from the analytical results, is the formula worked out by Babcock:

$$t = \left(\frac{100\,S - F\,S}{100 - 1.0753\,F\,S} - 1\right)(250 - 2.5\,F). \qquad \textbf{(6.)}$$

Where t = total solids not fat;
S = specific gravity of sample;
F = fat.

EXAMPLE.—Let the specific gravity S of a sample of milk be 1.03016 and the percentage of fat 3.33; what is the percentage of the total solids?

SOLUTION.—Substituting the known values, we obtain

$$t = \left[\frac{100 \times 1.03016 - (3.33 \times 1.03016)}{100 - (1.0753 \times 3.33 \times 1.03016)} - 1\right](250 - 2.5 \times 3.33).$$

$$t = \left(\frac{103.016 - 3.43043}{100 - 3.68874} - 1\right)(250 - 8.325).$$

$$t = (1.03399 - 1)(241.675).$$

$$t = .03399 \times 241.675 = 8.216.$$

Then, total solids not fat = 8.216, and fat = 3.33; hence, total solids = 8.216 + 3.33 = 11.546%. Ans.

ASH.

87. The residue from the determination of total solids is heated cautiously over the Bunsen burner, until a white ash is left. The results obtained in this manner are apt to be slightly low from loss of sodium chloride, etc.

88. Method of Association of Official Agricultural Chemists.—The method recommended by this association is as follows: In a weighed dish are placed 20 cubic centimeters of milk, to which 6 cubic centimeters of nitric acid are added; the whole is evaporated to dryness and ignited at a low, red heat until the ash is free from carbon.

FAT.

89. A large number of fat-extraction methods have been worked out and proposed, and it is here only possible to describe a few of the simpler ones.

90. Paper-Coil Method.—This method, which is also known, from its originator, as **Adam's method,** consists essentially in spreading the milk over absorbent paper, drying, and extracting the fat in an extraction apparatus; the milk is distributed in a very thin layer, and by a selective action of the paper the larger portion of the fat is left on the surface. It is essential that the paper contains no materials

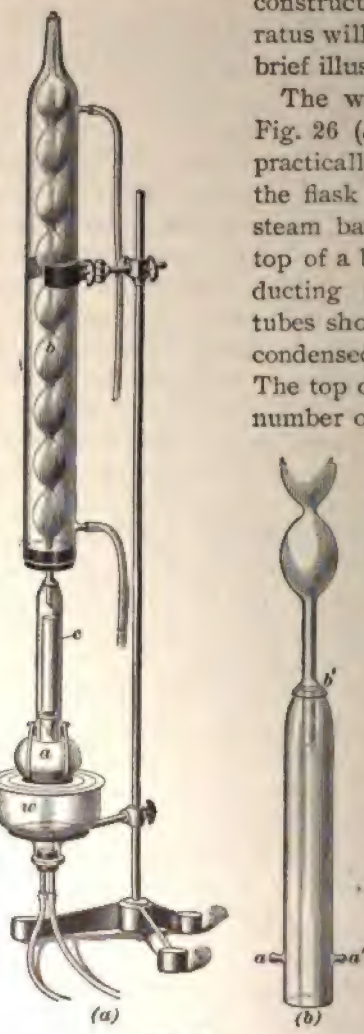
soluble in the liquid used for extraction. A paper, manufactured especially for this purpose by Schleicher and Schuell, is obtained in strips of suitable size.

The procedure is as follows: 5 cubic centimeters of the milk are discharged in a beaker 5 centimeters high and 3.5 centimeters in diameter. The charged beaker is weighed, and a strip of the paper, which has been rolled into a coil, thrust into it. In a few minutes, the paper will absorb nearly the whole of the milk. The coil is then carefully withdrawn, and stood, dry end downwards, on a watch glass. With a little practice, all but the last fraction of a drop will be absorbed by the paper. The beaker is again weighed and the weight of the milk taken is found by the difference. It is of importance to take up the whole of the milk from the beaker, as the paper has selective action, removing the watery constituents by preference over the fat. The charged paper is placed in the drying oven on a watch glass, milk end upwards, and dried. Usually an hour is sufficient. It is then inserted into the extraction tube of a Knorr continuous-extraction apparatus (see Fig. 26), the previously weighed flask *a* of which should have a capacity of about 150 cubic centimeters and contain about 75 cubic centimeters of anhydrous, alcohol-free ether, or petroleum spirit, boiling at about 45°. Heat is applied by means of the water bath. After the coil has received at least 10 to 12 washings, the flask is detached, the ether removed by distillation, and the fat dried by heating in an air oven at 105°. After cooling, the flask is wiped clean with a piece of silk, allowed to stand 10 minutes, and then weighed. Thimble-shaped cartridges made of fat-free paper are now made and are very convenient for holding the absorbent material on which the milk is spread; such a case may be used several times.

When the Babcock method (see Art. **85**) has been used, the cylinder and contents may be placed in the extraction tube and extracted as described.

91. Knorr's Continuous-Extraction Apparatus.—A large number of extraction apparatus have been constructed,

Knorr's extraction apparatus deserves preference, owing to its compactness, and the absence of stoppers, etc. The construction and operation of the apparatus will be readily understood by a brief illustrated description.



(a) (b)

FIG. 26.

The whole apparatus is shown in Fig. 26 (*a*), and it is seen that it is practically an upright condenser. *a* is the flask containing the solvent, *w* a steam bath made by cutting off the top of a bottle, inverting it, and conducting the steam into one of the tubes shown in the stopper, while the condensed water runs out of the other. The top of the bath is covered with a number of concentric copper rings, so that the opening may be made of any desirable size. *b* represents the condenser, which is a long glass tube, on which a number of bulbs have been blown, and which is attached to the hood *c* for holding the material to be extracted, as represented in Fig. 26 (*b*) at *b'*, making a solid glass union. Before joining the tube at *b'*, the rubber stopper, which is to hold it to the outside condenser of *b*, is slipped on.

A more detailed description of the different parts of the apparatus can be seen from consulting Figs. 27 and 28. In (*a*), Fig. 27, is represented a section of the flask that holds the solvent,

showing how the sides of the hood containing the material to be extracted pass over the neck of the flask. A view of the flask itself is shown in (*b*), Fig. 27. It is made by taking an ordinary flask, softening it about the neck and pressing the neck in so as to form a cup, as indicated in (*a*), to hold the mercury, which forms the union of the flask with the condenser. The flask is held in position by passing a rubber band below it, which is

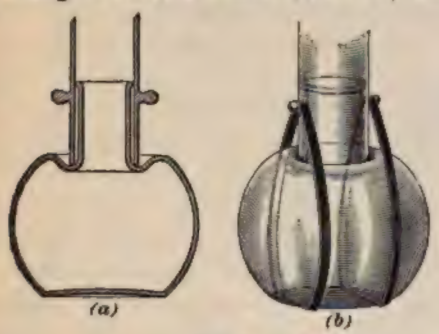


FIG. 27.

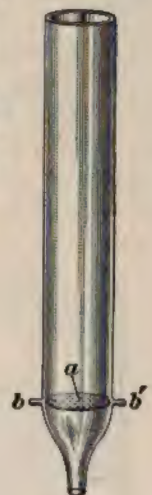


FIG. 28.

attached to the two glass nipples *a*, *a'*, shown in (*b*), Fig. 26. The material to be extracted may be contained in an ordinary tube, as shown in Fig. 28, which may be made from a test tube drawn out, as indicated in the illustration, having a perforated platinum disk sealed in at *a*. The containing tube rests on the edges of the flask containing the solvent, by means of nipples shown at *b*, *b'*.

92. Werner-Schmidt Method.—A very satisfactory and simple method for the determination of fat is that originated by Werner and Schmidt and recommended by Dr. Laffmann. It is especially suitable for sour milk.

Into a long test tube of 50 cubic centimeters capacity, graduated to tenths of cubic centimeters, 10 cubic centimeters of milk are measured and 10 cubic centimeters of strong hydrochloric acid added, or the milk may be weighed in a small beaker and washed into the tube with the acid. After mixing, the liquid is boiled $1\frac{1}{2}$ minutes, or the tube may be

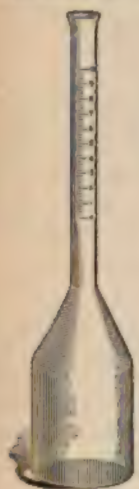
corked and heated in the water bath from 5 to 10 minutes, until the liquid turns brown; but it must *not* be allowed to turn black. The tube and its contents are cooled in water, 30 cubic centimeters of ether are then added, the whole shaken, and allowed to stand until the line of acid and ether is distinct. The cork is taken out and a double tube arrangement, as shown in Fig. 29, inserted. The stopper of this should be of cork, since it is rather difficult to slide the glass tube in a rubber one, and to avoid the possibility of the ether acting upon the rubber. The lower end of the exit tube *b* is adjusted so as to rest immediately above the junction of the two liquids. By blowing into *a*, the ethereal solution is blown out and received in a weighed flask. Two more portions of ether, 10 cubic centimeters each, are shaken with the acid liquid, blown out again, and added to the first. The ether is then distilled off and the fat dried and weighed.

FIG. 29.

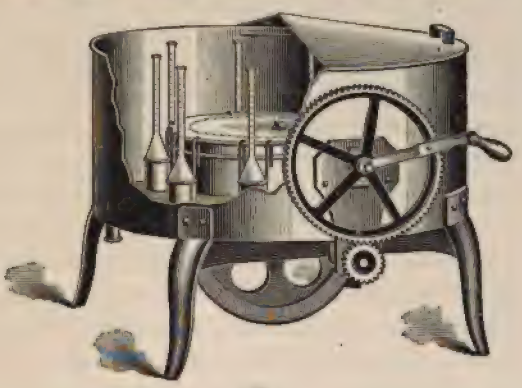
93. Babcock's Method.—Among the many quick volumetric methods that have been proposed for the determination of fat in milk, none has secured so wide an application as that suggested by Babcock.

The chief point of advantage in the use of this method is found in effecting the solution of the casein by means of sulphuric acid of about 1.83 Sp. Gr. By this reagent, the casein is dissolved in a few moments without the aid of any other heat than that generated by mixing the milk with the reagent. The bottle in which the separation is made is shown in (*a*), Fig. 30. The graduations on the neck are based on the use of 18 grams of milk. To avoid the trouble of weighing, the milk is measured from a pipette graduated

to deliver 18 grams of milk of the usual specific gravity. While it is true that normal milk may vary somewhat in its density, it has been found that a pipette marked 17.6 cubic centimeters delivers a weight that can be safely assumed to vary but slightly from the one desired. The graduated bottle holds easily 35 cubic centimeters in its expanded portion, and the volume of milk just noted is mixed with an equal volume of sulphuric acid. The complete mixture of the milk and acid is effected by gently rotating the flask until its contents are homogeneous. The final color of the mixture



(a)



(b)

FIG. 30.

varies from brown to black. While still hot, the bottles are placed in a centrifugal machine shown in (*b*), Fig. 30, and the whole whirled for at least 5 minutes. The revolutions should be at least between 700 and 1,000 per minute. After the expiration of 5 minutes, the bottles are taken out of the centrifuge and filled to the upper mark with hot water, replaced in the machine, and whirled again for 2 minutes. The fat will then be found in a clearly defined column in the graduated neck of the bottle. In reading the scale, the extreme limits between the lowest point marked by the lower meniscus and the highest point marked by the edge of the upper meniscus are to be regarded as the termini of the fat column.

TOTAL PROTEIDS.

94. Estimation of Total Proteid Matter.—This determination is most conveniently made by calculation from the figure for total nitrogen obtained by Gunning's modification of Kjeldahl's process. The reagents and apparatus required are as follows:

1. $\frac{n}{10}$ *sulphuric acid.*

2. $\frac{n}{10}$ *barium-hydrate solution.*

3. *Acid Potassium-Sulphate Solution.*—This solution is made by heating two parts of strictly chemically pure sulphuric acid with one part of chemically pure potassium sulphate, until the latter is entirely dissolved. The mixture is in a semisolid state, when cold, but may easily be liquefied by warming gently.

4. *A saturated solution of sodium hydrate.*

5. *Digestion and Distillation Flask.*—A flask should be chosen that has a capacity of about 600 cubic centimeters, and cylindrical neck about 18 centimeters long and 2.5 centimeters in diameter. It is supported on wire gauze and the mouth covered by inserting a funnel during the digestion. For distilling, a well fitting rubber stopper with delivery tube should be attached. The tube should be of the same diameter as the condensing tube, and should have one or two bulbs, about 4 centimeters in diameter, to prevent any solution being carried over by spurting. It should project slightly below the stopper and be cut obliquely.

6. *Condenser.*—The condensing tube should be of block tin, and have an external diameter of about 1 centimeter. At least 30 centimeters of its length should be in contact with the cooling water. The junction of the glass and tin tube is made by a short, close fitting rubber tube, and the tubes are so bent as to slope forwards toward the distilling flask. The lower end of the tin tube is connected by a short rubber tube with a glass bulb tube that dips below the surface of a measured volume (20 cubic centimeters) of the

standard sulphuric acid in an Erlemeyer flask of about 300 cubic centimeters capacity.

95. Five cubic centimeters of the milk are weighed or measured into the flask and evaporated to dryness over the water bath; 30 cubic centimeters of the acid potassium-sulphate mixture are added and heated over the Bunsen burner. At first, frothing occurs and white fumes escape, consisting chiefly of water vapor. To prevent loss of acid, the neck of the flask is fitted with a funnel that is covered with a watch glass. This will cause the acid to condense and run back into the flask. The operation is finished when the liquid is colorless, and generally requires about an hour. After it has cooled, about 200 cubic centimeters of distilled water and sufficient of the sodium-hydrate solution are added to make the mixture strongly alkaline. Forty to 50 cubic centimeters of the sodium-hydrate solution will be, as a rule, required for this purpose. It should be poured down the sides of the flask so that it does not mix at once with the acid. The flask is now connected with the condenser, and the contents mixed by shaking. The liquid is then distilled until the whole of the ammonium hydrate is collected, which will usually be the case when about 150 cubic centimeters have passed over. The receiver and short tube dipping in it are then detached, and the distillate titrated to determine the amount of acid neutralized. From this, the amount of ammonium hydrate is calculated, and the nitrogen in this multiplied by 6.38 will give the figure for the total proteids.

The Association of Official Agricultural Chemists recommends an indicator prepared as follows: 3 grams of cochineal are digested for several days in a mixture of 50 cubic centimeters of strong alcohol and 200 cubic centimeters of water. After being filtered, the solution is ready for use.

96. Determination of Total Proteids by Copper Sulphate.—This method, which is due to Ritthausen, depends on precipitation by copper sulphate and sodium hydrate. The reagents required are as follows:

1. *Copper Sulphate Solution.*—Pure crystallized copper sulphate, to the amount of 34.639 grams, is dissolved in distilled water, and the solution made up to 500 cubic centimeters.

2. *Sodium Hydrate Solution.*—A suitable solution is prepared by dissolving 12 grams of $NaOH$ in 500 cubic centimeters of water.

Ten grams of the milk are placed in a beaker, diluted with 100 cubic centimeters of distilled water, 5 cubic centimeters of the copper-sulphate solution added by means of a pipette, and the whole thoroughly mixed. While constantly stirring, the sodium-hydrate solution is then carefully added drop by drop, until the precipitate settles quickly and the solution becomes neutral. Great care should be exercised to avoid any excess of the alkali, as an excess prevents the complete precipitation of the proteids. When the operation is correctly performed, which requires little practice, the precipitate, which includes the fat, settles quickly, and carries down all the copper. The mixture is poured into a filter, previously dried at 130°, and weighed; the precipitate is washed with hot water, first by decantation, and then on the filter. The filtrate and washing are set aside for the determination of sugar, as described later, and the precipitate washed with alcohol to remove all traces of water, and dried. The fat is then removed from the dry precipitate by extraction with ether, as has been previously described; the residue is dried and weighed, then transferred to a porcelain crucible, incinerated, and again weighed. The weight of the filter and contents, less that of the filter and residue after ignition, gives the weight of the proteids. The results are slightly high.

CASEIN AND ALBUMIN.

97. Official Method for Determination of Casein.—The determination of casein in milk should be made when the milk is fresh, or, at least, nearly so. If it is not possible to make this determination within the first 24 hours after the milking, 1 part of formaldehyde should be added to every 2,500 parts of milk, and the whole kept in a cool place.

Ten grams of milk are placed in a beaker, and 90 cubic centimeters of water, having a temperature of 40° to 42°, are added. To this, 1.5 cubic centimeters of a solution containing 10 per cent., by weight, of acetic acid are added, the whole stirred with a glass rod and then allowed to stand from 3 to 5 minutes. The supernatant liquid is then decanted through the filter, the precipitate washed 2 or 3 times by decantation with a moderate quantity of cold water, and finally transferred to the filter, and washed on the filter twice. The filtrate should be clear, or nearly so. Should it not be clear when it first runs through, it can generally be made so by two or three repeated filtrations, after which the washing of the filtrate can be completed.

The washed precipitate and filter are transferred to the flask used in Gunning's modification of Kjeldahl's method for the determination of nitrogen, and the nitrogen determined as explained in Art. **94.** The nitrogen thus obtained, multiplied by 6.38, gives the amount of casein in the sample.

In working with milk that has been kept with a preservative, the acetic acid should be added in small proportions, a few drops at a time, while stirring, and the addition continued until the liquid above the precipitate becomes clear, or very nearly so.

98. Official Method for the Determination of Albumin.—The filtrate obtained in the determination of casein is neutralized with caustic alkali, $\frac{3}{10}$ cubic centimeter of a 10-per-cent. solution of acetic acid added, and the mixture heated to the temperature of boiling water for from 10 to 15 minutes. The precipitate is collected on a filter, washed 2 or 3 times with cold water, and the nitrogen determined therein in exactly the same way as indicated in Art. **95.** The nitrogen thus obtained, multiplied by 6.38, gives the amount of albumin present in the sample.

99. Remaining Nitrogen Compounds.—The remaining compound or compounds of nitrogen are determined by difference, subtracting from the amount of total nitrogen compounds the sum of the casein and albumin.

SUGAR.

100. Soxhlet's Method.—The following method, due to Soxhlet, employs a Fehling's solution, made as required, by mixing equal parts of the following solutions:

Copper-Sulphate Solution.—Pure crystallized copper sulphate, to the amount of 34.639 grams, is dissolved in distilled water and made up to 500 cubic centimeters.

Alkaline-Tartrate Solution.—Pure sodium-potassium tartrate, equal to 173 grams, and 51 grams of pure sodium hydrate are dissolved and the solution made up to 500 cubic centimeters.

Of the mixed filtrate obtained in the determination of total proteids by Ritthausen's method (see Art. **96**), 100 cubic centimeters are boiled, and 50 cubic centimeters of boiling Fehling's solution added, and the boiling of the mixture continued for exactly 6 minutes. The precipitate is allowed to settle, and the heating continued for 2 minutes, after which the precipitate is brought on a filter, washed three times with boiling water, twice with alcohol, and finally with ether. The filter and precipitate are then dried, the latter removed to a watch glass, and the filter burned in a porcelain crucible, whose weight has been previously ascertained. The precipitate is added, and the cuprous oxide converted into cupric oxide by strong ignition over a Bunsen burner for about 10 minutes.

The amount of copper reduced under these conditions is not directly proportional to the milk sugar present. Table 3 shows the amount of milk sugar $C_{12}H_{22}O_{11}, H_2O$ equivalent to the given weights of cupric oxide. The volumes of Fehling's solution and sugar solution must conform strictly to the figures here given.

The figures given in Table 3 are the weights of copper and lactose. The equivalent weights of copper and cupric oxide are almost exactly in the ratio of 4 to 5; hence, to obtain the weight of copper from that of cupric oxide in the above determination, we need only multiply the weight of cupric oxide by .8.

For the amounts of copper intermediate between those given in the table, the quantity of lactose is determined by the factor in the third column, which represents the weight of copper corresponding to 1 milligram of lactose at that point. If, for instance, 178 milligrams of copper are obtained, the calculation will be as follows:

$$\begin{aligned} 175 \text{ milligrams } Cu &= 127.80 \\ 3 \text{ milligrams } Cu \times .75 &= \underline{\quad 2.25} \\ 178 \text{ milligrams } Cu &= 130.05 \text{ mm. } C_{12}H_{22}O_{11}, H_2O. \end{aligned}$$

TABLE 3.

WEIN'S TABLE FOR EQUIVALENT WEIGHTS OF LACTOSE, CALCULATED FOR USE IN SOXHLET'S METHOD.

Copper.	Lactose.	Factor.	Copper.	Lactose.	Factor.	Copper.	Lactose.	Factor.
120	86.4	.73	215	158.2	.76	310	232.2	.81
125	90.1	.73	220	161.9	.76	315	236.1	.81
130	93.8	.74	225	165.7	.76	320	240.0	.81
135	97.6	.74	230	169.4	.76	325	243.9	.81
140	101.3	.74	235	173.1	.76	330	247.7	.82
145	105.1	.74	240	176.9	.76	335	251.6	.82
150	108.8	.74	245	180.8	.77	340	255.7	.82
155	112.6	.75	250	184.8	.77	345	259.8	.82
160	116.4	.75	255	188.7	.78	350	263.9	.82
165	120.2	.75	260	192.5	.78	355	268.0	.82
170	123.9	.75	265	196.4	.78	360	272.1	.82
175	127.8	.75	270	200.3	.79	365	276.2	.82
180	131.6	.75	275	204.3	.80	370	280.5	.85
185	135.4	.76	280	208.3	.80	375	284.8	.85
190	139.3	.76	285	212.3	.80	380	289.1	.85
195	143.1	.76	290	216.3	.80	385	293.4	.85
200	146.9	.76	295	220.3	.80	390	297.7	.85
205	150.7	.76	300	224.4	.81	395	302.0	.85
210	154.5	.76	305	228.3	.81	400	306.3	.85

ANALYSIS OF BUTTER.

PRELIMINARY REMARKS.

101. Butter, a mixture of fat, water, and curd, is obtained by churning cream from cow's milk. The water contains, in solution, milk sugar and the salts of milk. Common salt is usually present, being added after the churning, and artificial coloring is frequently used.

The composition of butter usually varies within the following limits: Fat, 78 to 94 per cent.; curd, 1 to 3 per cent; water, 5 to 14 per cent.; and salt, 0 to 7 per cent.

102. Nostrums for Butter Making.—Preparations are sold purporting to possess the property of increasing the yield of butter from a given quantity of milk. These preparations are simply made up to deceive, and mostly contain rennet or pepsin, salt, and very often annatto. These ingredients curdle the milk, and allow the incorporation of much cheese and water with the butter, hence the increased yield, at the expense of the quality of the butter.

Samples of butter have thus been met that contained as much as 40 per cent. of water, while it is generally considered that the maximum amount of water should not exceed 16 per cent. Butter containing an excess of water quickly turns rancid, and has a spongy and, unless artificially colored, pale appearance.

103. Sampling of Butter.—If large quantities of butter are to be sampled, a butter trier, or sampler, may be used. The portions thus drawn, about 500 grams, are to be perfectly melted in a closed vessel at as low a temperature as possible, and when melted the whole is to be shaken violently for some minutes until the mass is homogeneous, and sufficiently solidified to prevent the separation of the fat and water. A portion is then poured out into the vessel from which it is to be weighed for analysis, and should nearly or quite fill it. The sample should be kept in a cold place until analyzed.

ANALYTICAL PROCESSES.

104. The following methods for the analysis of butter have been adopted by the Association of Official Agricultural Chemists:

105. Determination of Water.—From 1.5 to 2.5 grams of butter are dried to constant weight at the temperature of boiling water in a flat-bottomed glass dish having a surface of at least 20 square centimeters. The use of clean, dry sand or asbestos with the butter is admissible, and is necessary if a dish with round bottom should be employed.

106. Determination of Fat.—The dry butter from the above water determination is dissolved in the dish with absolute ether, or with 76° petroleum spirit. The contents of the dish are then transferred to a Gooch crucible with the aid of a wash bottle filled with the solvent, and are washed until free from fat. The crucible and contents are heated at the temperature of boiling water until the weight is constant. The weight of fat is represented by the loss of weight of the dried butter.

107. Determination of Casein and Ash.—The Gooch crucible containing the residue from the fat determination, consisting of casein and salts, is covered and heated, gently at first, gradually raising the temperature to just below redness. The cover may then be removed and the heat continued until the contents of the crucible assumes a white color. The loss in weight of the crucible and contents represents the weight of the casein, and the residue in the crucible, ash, or mineral matter.

108. Determination of Salt.—It is the usual custom in the manufacture of butter in this country, to add, as a condiment, a certain proportion of salt. A convenient method of determining the quantity of salt is found in the removal thereof, from the sample, by repeated washing with hot water, and determining the salt in the wash water by titration with silver nitrate. The operation is conducted as follows:

From 5 to 10 grams of the sample are placed in a separatory funnel, hot water added, the stopper inserted, and the contents of the funnel well shaken. After standing until the fat has all collected on top of the water, the stop-cock is opened and the water is allowed to run into an Erlemeyer flask, being careful to let none of the fat globules pass. Hot water is again added to the sample, and the extraction is repeated several times, using each time from 10 to 20 cubic centimeters of water. The resulting washings contain all but a mere trace of the sodium chloride originally present in the butter. The sodium chloride is determined in the filtrate volumetrically by means of $\frac{n}{10}$ silver nitrate, using potassium chromate as an indicator.

SUBSTITUTES AND ADULTERANTS OF BUTTER.

109. In this country, butter is never adulterated with cocoa or sesame oil, as is sometimes the case in European countries. The common substitute for butter here is oleomargarine, and the most common butter adulterant, neutral lard. The term *oleomargarine* includes now, by Act of Congress, any oleaginous substance intended as a substitute for butter, containing any proportion of fat other than butter fat. The principal materials employed in the preparation of butter substitutes are cottonseed oil, beef fat, and mutton fat.

110. When fats are saponified, and the soap treated with acid, the individual fatty acids are obtained. It is upon the recognition of the peculiar acid radicals existing in butter that the most satisfactory method of distinguishing it from other fats is based. Since the relative proportion of the radicals differs in different samples, the quantitative estimation cannot be made with accuracy, but when the foreign fats are substituted to the extent of 25 per cent. or more, the adulteration can be detected with certainty and an approximate quantitative determination made.

DETERMINATION OF VOLATILE ACIDS.

111. Leffmann and Beam's Distillation Method.—The fatty acids containing a small number of carbon atoms, set free by the process noted above, are soluble in water and volatile. A method for their estimation, depending on their solubility in water, was perfected by Hehner, but has now been displaced by a distillation method originally suggested by Hehner and Angell, but improved by Reichert and Wollny, and modified by Leffmann and Beam.

For this method, the following reagents are required:

Glycerol Soda.—Pure sodium hydrate, to the amount of 100 grams, is dissolved in 100 cubic centimeters of water, and allowed to stand until clear. Of this solution, 20 cubic centimeters are mixed with 180 cubic centimeters of pure concentrated glycerol.

Sulphuric Acid.—This reagent consists of 20 cubic centimeters of chemically pure concentrate sulphuric acid, made up with distilled water to 1 liter.

Barium Hydrate.—This reagent consists of an accurately standardized $\frac{n}{10}$ barium-hydrate solution.

Indicator.—An alcoholic solution of phenol phthalein is used as an indicator.

About 50 grams of butter are placed in a beaker, and heated to a temperature of 50° to 60°, until the water and the curd have settled to the bottom. The clear fat is then poured on a warm, dry, plaited filter, and kept in a warm place until 25 or 30 cubic centimeters have been collected. If the filtrate is not perfectly clear, it should be reheated for a short time and again filtered.

A 300-cubic-centimeter flask is washed thoroughly, rinsed with alcohol, and then with ether, and thoroughly dried by heating in the drying oven. After cooling, it is allowed to stand for about 15 minutes, and weighed.

A pipette, graduated to 5.75 cubic centimeters, is heated to about 60°, and filled to the mark with the well mixed fat, which is then run into the flask. After standing for about 15 minutes, the flask and contents are weighed; 20 cubic

centimeters of the glycerol soda are added, and the flask heated over the Bunsen burner. The mixture will foam more or less, but this may be controlled, and the operation accelerated, by shaking the flask. When all the water has been driven off, the liquid will cease to boil, and if the heat and agitation be continued for a few moments, complete saponification will be effected, the mixture becoming perfectly clear. The whole operation, exclusive of weighing the fat, requires less than 5 minutes. The flask is then withdrawn from the heat and the soap dissolved in 135 cubic centimeters of water. The first portion of water should be added drop by drop, and the flask shaken between each addition in order to avoid foaming. When the soap is dissolved, 5 cubic centimeters of the dilute sulphuric acid are added, a piece of pumice stone dropped in, and the liquid distilled until 110 cubic centimeters have been collected in a flask that is accurately graduated to that volume.

The arrangement of the apparatus for the distillation is shown in Fig. 31, and needs no further explanation. The

FIG. 31.

flame should be so regulated that the above mentioned volume is collected within 30 minutes.

The 110 cubic centimeters of distillate, after thorough mixing, are filtered through a perfectly dry filter; 100 cubic centimeters of the filtered distillate are poured into a beaker having a capacity of from 200 to 250 cubic centimeters, .5 cubic centimeter of phenol-phthalein solution added, and decinormal barium hydrate run in until a red color is just produced. The contents of the beaker are then returned to the measuring flask, to remove any acid remaining therein, poured again into the beaker, and the titration continued until the red color produced remains permanent for 2 or 3 minutes.

A blank experiment should be made to determine the amount of decinormal alkali required by the reagents required. With a good quality of glycerol, this will rarely exceed .5 cubic centimeter.

As a rule, 5 grams of butter yield a distillate that requires from 24 to 34 cubic centimeters of decinormal alkali solution, although several instances have been published in which genuine butter has given a figure as low as 22.5 cubic centimeters; such results are, however, very exceptional. The materials employed in the preparation of oleomargarine yield a distillate requiring usually less than 1 cubic centimeter of the decinormal barium-hydrate solution for neutralization. Commercial oleomargarine is, however, usually churned with milk, in order to secure a genuine butter flavor, and consequently acquires a small amount of butter fat; hence, the distillate of commercial oleomargarine usually requires from 1 to 2 cubic centimeters of barium-hydrate solution.

112. Method of Association of Official Agricultural Chemists.—For the method of determining the volatile acids, adopted by the Association of Official Agricultural Chemists, the following reagents are required:

Sodium-Hydrate Solution.—Chemically pure sodium hydrate, to the amount of 100 grams, is dissolved in 100 cubic centimeters of water. The sodium hydrate should be as free as possible from carbonates, and be preserved out of contact with the air.

Alcohol.—This reagent consists of alcohol of about 95 per cent. strength, redistilled with caustic soda.

Acid.—This reagent is a solution of sulphuric acid containing 200 cubic centimeters of strongest sulphuric acid in 1,000 cubic centimeters of water.

Barium-Hydrate Solution.—This reagent consists of an accurately standardized, approximately decinormal, solution of barium hydrate.

Indicator.—The indicator is a solution of 1 gram of phenolphthalein in 100 cubic centimeters of alcohol.

Saponification Flask.—This flask is made of hard, well annealed glass, capable of resisting the tension of alcohol vapor at 100°, and having a capacity of from 250 to 300 cubic centimeters.

Pipettes.—One pipette graduated to deliver 40 cubic centimeters, and another to deliver 5.75 cubic centimeters.

Distilling Apparatus.—An apparatus similar to that shown in Fig. 31.

Burette.—An accurately calibrated burette reading to tenths of a cubic centimeter.

The method of determining is as follows: The butter or fat to be examined should be melted, and kept in a dry, warm place at about 60° for 2 or 3 hours, until the water and curd have entirely settled out. The clear supernatant fat is poured off and filtered through dry filter paper, in a jacketed funnel containing hot water, as shown in Fig. 32. Should the filtered fat, in a fused state, not be perfectly clear, it must be filtered a second time.

FIG. 32.

The saponification flasks are prepared by having them thoroughly washed with water, alcohol, and ether, wiped perfectly dry on the outside, and heated for 1 hour at the temperature of boiling water. The flasks

should then be placed on a tray by the side of the balance, and covered with a silk handkerchief until they are perfectly cool. They must not be wiped with a silk handkerchief within 15 or 20 minutes of the time they are weighed. The weight of the flask having been accurately determined, they are charged with the fat in the following way:

A pipette, with long stem, marked to deliver 5.75 cubic centimeters, is warmed to a temperature of about 50°. The fat having been poured back and forth once or twice into a dry beaker, in order to thoroughly mix it, is taken up in the pipette and the nozzle of the pipette carried to near the bottom of the flask, having been previously wiped to remove any adhering fat, and 5.75 cubic centimeters of fat allowed to flow into the flask. After the flask has thus been charged, it should be recovered with a silk handkerchief and allowed to stand 15 or 20 minutes, when it is again weighed.

Then, 10 cubic centimeters of 95-per-cent. alcohol are added to the fat in the flask, and 2 cubic centimeters of the sodium-hydrate solution; a soft cork stopper is now inserted in the flask and tied down with a piece of twine. The saponification is then completed by placing the flask upon the water or steam bath. The flask during saponification, which should last 1 hour, should be gently rotated from time to time, being careful not to project the soap for any distance upon its sides. At the end of 1 hour the flask, after having been cooled to near the temperature of the room, is opened. The stopper having been laid loosely in the mouth of the flask, the alcohol is removed by dipping the flask into the steam bath. The steam should cover the whole of the flask except the neck. After the alcohol is nearly removed, frothing may be noticed in the soap, and to avoid any loss from this cause, or any creeping of the soap up the sides of the flask, it should be removed from the bath and shaken to and fro until the frothing disappears. The last traces of alcohol vapor may be removed from the flask by waving it briskly, mouth down, to and fro. After the removal of the alcohol, the soap should be dissolved by adding 135 cubic centimeters

of recently boiled distilled water, warming on the steam bath with occasional shaking, until solution of the soap is complete. When the soap solution has cooled to about 65°, the fatty acids are separated by adding 5 cubic centimeters of the dilute sulphuric-acid solution mentioned previously. The flask should now be restoppered as in the first instance, and the fatty-acid emulsion melted by replacing the flask on the steam bath. According to the nature of the fat under examination, the time required for the fusion of the fatty-acid emulsion may vary from a few minutes to several hours.

After the fatty acids are completely melted, which can be determined by their forming a transparent, oily layer on the surface of the water, the flask is cooled to the temperature of the room, and a few pieces of pumice stone added. The pumice stone is prepared by throwing it, at a white heat, into distilled water, and keeping it under water until used. The flask is now connected with a glass condenser, slowly heated with a naked flame, until ebullition begins, and then the distillation continued by regulating the flame in such a way as to collect 110 cubic centimeters of the distillate in, as nearly as possible, 30 minutes. The distillate should be received in a flask accurately graduated at 110 cubic centimeters.

The 110 cubic centimeters of the distillate, after thorough mixing, are filtered through a dry filter paper and collected in a flask marked at 100 cubic centimeters. These 100 cubic centimeters of the filtered distillate are poured into a beaker holding from 200 to 250 cubic centimeters, .5 cubic centimeter of the phenol-phthalein solution added, and decinormal barium-hydrate solution run in until a red color is produced. The contents of the beaker are then returned to the 100-cubic-centimeter measuring flask, to remove any acid remaining therein, poured again into the beaker, and the titration continued until the red color produced remains apparently unchanged for 2 or 3 minutes. The number of cubic centimeters of decinormal barium hydrate required should be increased by one-tenth.

DETECTION OF BUTTER ADULTERATION BY ACETIC ACID.

113. Many other methods of detecting butter adulteration have been proposed; the distinction between butter and its adulterants is, however, not so distinct in the various methods proposed as it is in the distillation method described in the preceding articles. It is not possible to give all of these methods, and the student must refer to a book on agricultural chemistry, if he wishes information on this point. Only one, known as *Valenta's test*, will here be given.

114. Valenta's Test.—This simple test depends on the behavior of butter and acetic acid, and is the one of most value. The strength of the acetic acid may vary, but it must always be standardized against a sample of pure butter fat.

In a dry test tube are placed 3 cubic centimeters of the melted fat, and an equal volume of acetic acid added, and the mixture heated until solution has taken place. It is then allowed to cool spontaneously, and the temperature noted at which the liquid begins to get turbid.

After a large number of experiments, it has been found that an acetic-acid solution of 95.5 per cent. is the most efficient.

With an acid of such a strength, the following figures have been obtained:

Butter fat (24 samples).

Highest	39°.
Lowest	29°.
Mean	36°.

Oleomargarine (5 samples).

Highest	97°.
Lowest	94°.
Mean	95°.

Cottonseed oil, various samples	71°, 75°, 71°, 85°, 86°, 88°, 89°.
Peanut oil	72°, 73°.
Lard oil	75°, 76°, 75°.
Lard	98°, 97°, 98°, 97°.
Beef stearin	100°.
Lard stearin	100°.

Attention should be called to the fact that the presence of moisture in the fat is one of the most fruitful sources of error, and that it is generally recommended to filter the sample through dry filter paper before mixing with the acetic acid.

BUTTER COLORS AND THEIR DETECTION.

115. Where cows are deprived of green food and root crops, such as carrots, and kept on poorly balanced rations, the butter made from their milk may be almost colorless. To remedy this defect, it is quite common practice to color the product artificially. Almost the sole coloring matter used in this country is annatto. Other coloring matters that are occasionally employed are turmeric, saffron, marigold leaves, yellow wood (*Chlorophora tinctoria*), carrot juice, chrome yellow (lead chromate), and dinitrocresol.

The use of small quantities of turmeric or saffron is unobjectionable from a sanitary point; that of annatto, to say the least, is offensive to the esthetic sense, stale urine being employed in its manufacture, while such a coloring substance as lead chromate is certainly dangerous to the health.

The detection of annatto or saffron in butter may be accomplished by the method of *Cornwall.*

116. Cornwall's Method for the Detection of Annatto and Saffron in Butter.—About 5 grams of warm and filtered fat are dissolved in about 50 cubic centimeters of ordinary ether, in a wide tube, and the solution vigorously shaken from 10 to 15 seconds, with from 12 to 15 cubic centimeters of a very dilute solution of caustic potash or soda in water, only alkaline enough to give a distinct reaction with turmeric paper, and to remain alkaline after separating from the ethereal fat solution. The corked tube is set aside, and in a few hours, at most, the greater part of the aqueous solution, now colored more or less yellow by the annatto, can be drawn from beneath the ether with a pipette in a sufficiently clear state to be evaporated to dryness, and tested with a drop of concentrated sulphuric acid.

Sometimes it is well to further purify the aqueous solution by shaking it with some fresh ether before evaporating it, and any fat globules that may float on its surface during evaporation should be removed by touching them with a slip of filter paper; but the solution should *not* be filtered, because the filter paper may retain much of the coloring matter.

The dry yellow or, perhaps, slightly orange residue turns, in the presence of annatto, blue or violet-blue with sulphuric acid, then quickly green, and finally brownish or somewhat violet, this final change being variable, according to the purity of the extract.

Saffron can be extracted in the same way; it differs from annatto very decidedly, the most important difference being the absence of the green coloration.

Genuine butter, free from foreign coloring matter, imparts at most a very pale-yellow color to the alkaline solution; but it is important to note that a mere green coloration of the dry residue, on addition of sulphuric acid, is not a certain indication of annatto, because the writer has thus obtained from genuine butter, free from foreign coloring matter, a dirty green coloration, but *not* preceded by any blue or violet tint.

117. Turmeric is easily identified by the brownish to reddish stratum that forms between the ethereal fat solution and the alkaline solution before they are intimately mixed. It may be even better recognized by carefully bringing a feeble alkaline solution of ammonia in alcohol beneath the ethereal fat solution with a pipette, and gently agitating the two, so as to mix them partially.

EXAMINATION OF FERTILIZERS.

PRELIMINARY REMARKS.

118. Fertilizers are manufactured by the mixing of various forms of refuse materials from other industries, where such material contain either nitrogen or phosphoric acid, or both, such as sugar scums, refuse from slaughter houses, fat melting, glue making, tanning, etc. The

principal source of phosphoric acid is the phosphate rock from the southern states, which, in pulverulent form, is mixed in suitable proportions with materials more or less rich in nitrogen, and then treated with sulphuric acid to render most of the phosphoric acid available, chiefly in form of calcium superphosphate. Inevitably, the finished fertilizers in the market contain more or less of what is called "reduced," "inverted," or "reverted" phosphate, which is not readily soluble in water alone, but dissolves in solutions of several organic salts, and under some conditions, is available for the purposes of fertilization of plant crops. For some purposes, the addition of potassium salts to the fertilizer is necessary. These are usually added in the form of chloride or sulphate, which, under the name of **Stassfurt salts,** are largely imported for that purpose.

119. Preparation of Sample.—The sample should be well mixed, finely ground, and passed through a sieve having circular perforations 1 millimeter in diameter. The grinding and sifting should be performed as rapidly as possible, to avoid loss or gain of moisture during the operation.

DETERMINATION OF MOISTURE.

120. As the percentage of moisture in a fertilizer may vary considerably under the conditions to which it is exposed, a determination of moisture is always necessary, in order that the results on other constituents, as determined by different analysts, as, for instance, those of the buyer and seller, may be fairly compared.

Some analysts invariably heat to a certain temperature (100° or 110°) until a constant weight is obtained; others heat for a certain time, 2, 3, or 5 hours, and call the loss *moisture*. The following plan, prescribed by the Association of Official Agricultural Chemists, is, however, probably most uniformly followed.

Potash salts, sodium nitrate, and ammonium sulphate are heated in quantities of 1 to 5 grams at about 130° until the

weight is constant, and the loss of weight is considered moisture. Of all other fertilizers, 2 grams, or, should the sample be very coarse, 5 grams, are heated at 100° for 5 hours, and the loss considered moisture.

DETERMINATION OF PHOSPHORIC ACID.

121. The phraseology regarding phosphoric acid in fertilizers is not always as exact as might be desirable. From what has been stated in Art. **118,** various forms of phosphoric acid are considered to exist, and, in fact, three forms are generally recognized in fertilizers, namely: (1) That readily soluble in water, consisting presumably of calcium superphosphate $CaH_4(PO_4)_2$. This is generally known as *soluble phosphoric acid*, or *water-soluble phosphoric acid.* (2) That not readily soluble in water, but soluble in certain organic solutions, presumably consisting of $CaH(PO_4)$, or acid ferric and aluminic phosphates. This form is usually called *reverted*, *inverted*, *reduced*, etc., *phosphoric acid;* or, because it is usually determined by washing it out with solution of ammonium citrate, it has been called *citrate soluble phosphoric acid.* (3) That insoluble both in water and in the solvents for (2), remaining presumably in the condition in which it originally existed in the phosphate rock, $Ca_3(PO_4)_2$. This form is either called *insoluble phosphoric acid* or *citrate insoluble phosphoric acid.*

The sum of (1) and (2) is usually termed *available phosphoric acid*, although English chemists apply the term "available" as a synonym for "water soluble," and, on the other hand, the term "soluble phosphoric acid" is sometimes used when the sum of (1) and (2) is meant.

Much of this confusion of terms has arisen from the diversity of opinion as to the utility of these different forms in which the phosphoric acid may be combined. The sum of (1), (2), and (3) is called *total phosphoric acid.*

122. Total Phosphoric Acid.—The phosphoric acid is usually separated as the molybdate compound, which is

dissolved in ammonia, and precipitated for weighing by magnesia mixture.

As the organic matter of the fertilizer would interfere with the complete separation of the phospho-molybdate, it must be destroyed (usually by the ignition with or without the addition of some nitrate). Hydrochloric acid is the best solvent for ignited phosphates, but the molybdate precipitation is best made in a nitric-acid solution, so that, although, after ignition, hydrochloric acid must be used to effect solution, nitric acid and nitrates should largely predominate when the molybdate separation is effected.

Weigh out 2 grams of the dried sample into a platinum dish and moisten these with 5 cubic centimeters of a magnesium-nitrate solution, made by dissolving 600 grams of magnesium nitrate in 1,000 cubic centimeters of water, and ignite. After cooling, add 5 to 10 cubic centimeters of hydrochloric acid and transfer the whole to a beaker; add 30 cubic centimeters of nitric acid, boil for a few moments, and filter.

When the fertilizers contain much iron and aluminum, more hydrochloric acid should be used. If made up with phosphatic slags, gelatinous silica will appear, which requires evaporation to dryness, and taking up with hydrochloric acid.

A method recommended for fertilizers containing very large quantities of organic matter, consists in boiling with 20 to 30 cubic centimeters of concentrate sulphuric acid in a Kjeldahl flask, adding 4 grams of sodium nitrate at the beginning of the digestion and a small quantity after the solution has become nearly colorless. After the solution is entirely without color, add 150 cubic centimeters of water, boil for a few minutes, and dilute. The presence of hydrochloric or sulphuric acid, however, retards the precipitation of the molybdate, and is best avoided, if possible. Hydrochloric acid can be removed by evaporating low with excess of nitric acid; sulphuric acid, however, cannot.

In any case, dilute the solution to 250 cubic centimeters, mix well, and remove, by means of a pipette, 50 cubic centimeters to a clean beaker for the analysis, this representing

.4 gram of the original sample. Add ammonia until it is just alkaline, then acidify by addition of 5 cubic centimeters of nitric acid; add 10 to 15 grams of crystallized ammonium nitrate, warm to about 85°, and add molybdate solution in the proportion of 50 cubic centimeters for every .01 gram of phosphoric acid assumed to be present. For ordinary fertilizers that contain less than 20 per cent. P_2O_5, 50 cubic centimeters will be quite sufficient. Digest for about an hour at 65° with frequent stirring, filter and wash with a cold dilute solution of ammonium nitrate, acidified with nitric acid. Test the filtrate for phosphoric acid by renewed digestion and addition of molybdate solution. Dissolve the precipitate on the filter with ammonia and hot water, and wash into a beaker to a bulk of not more than 100 cubic centimeters. Nearly neutralize this with hydrochloric acid, cool, and add magnesia mixture from a burette, slowly, about 1 drop per second, stirring vigorously. Let the whole stand for 15 minutes, and add 30 cubic centimeters of ammonia solution of .96 Sp. Gr. Let it stand for some time (2 hours is usually sufficient), and then filter and wash thoroughly with 2.5 per cent. NH_3, until practically free from chlorides. Burn the filter in a crucible, add the precipitate, ignite to whiteness, cool in a desiccator, and weigh as $Mg_2P_2O_7$.

123. Water-Soluble Phosphoric Acid.—Place 2 grams of the dry sample on a 9-centimeter filter, wash with successive small portions of water, allowing each portion to run through the filter before adding a new one, until the filtrate measures about 250 cubic centimeters. If the filtrate be turbid, add a little nitric acid. Make up to any convenient definite volume, mix well, remove 50 cubic centimeters and determine the phosphoric acid exactly as described in the preceding article.

124. Citrate, Soluble or Reduced, Etc., Phosphoric Acid.—Take 2 grams of the sample, wash out the "water-soluble" phosphoric acid as described in Art. **123**, and then rinse the residue into a 200-cubic-centimeter flask by use

of 100 cubic centimeters of absolutely neutral ammonium citrate solution of 1.09 Sp. Gr. Stopper tightly with a smooth rubber stopper, and place the flask in a water bath, and maintain it at such a temperature that the contents of the flask will stand at exactly 65° for exactly 30 minutes; then filter rapidly, and wash thoroughly with water at 65°. The "reduced" phosphoric acid is by this means removed and determined in the usual manner. It will, however, be more convenient to determine it indirectly by igniting the filter paper and contents, and carrying through the determination on the portion undissolved. The sum of the water-soluble and citrate-insoluble subtracted from the total phosphoric acid, gives the citrate-soluble phosphoric acid.

125. Preparation of Ammonium-Citrate Solution. Ammonium-citrate solution is prepared by dissolving 370 grams of commercial citric acid in 1,500 cubic centimeters of water, nearly neutralizing this with commercial ammonia, and cooling. After cooling, more ammonia is added, until the solution is exactly neutral, when the volume is made up to 2 liters. This solution should have a specific gravity of 1.09 at 20°.

DETERMINATION OF NITROGEN.

126. Nitrogen is found in fertilizers both in the form of ammonia (potential and actual) and as nitrate. By potential ammonia is meant the nitrogen that, by the progress of decomposition of the organic matter of the fertilizer when in use, will develop ammonia. The nitrogen may be determined by one of the following methods:

127. Dumas's Method.—A definite amount of the sample is mixed with copper oxide in a combustion tube closed at one end, containing at the closed end a quantity of pure sodium bicarbonate, which furnishes a supply of carbon dioxide with which to sweep out first the air and finally the products of the combustion from the tube. A roll of bright copper gauze is introduced at the open end to prevent the

escape of any nitrogen in the form of oxides of nitrogen. The tube is closed with a cork and delivery tube, and the nitrogen is collected in a measuring tube over caustic potash, whereby the carbon dioxide is removed.

A piece of combustion tube is drawn off and sealed at one end before the blowpipe. The tube should be about 76 centimeters long, or of such length that it can be heated to the extreme end when in the combustion furnace.

A quantity of chemically pure, dry sodium carbonate is introduced, so that when the closed end is gently tapped on the bench, the salt shall occupy a space of about 20 centimeters. A layer of about 12 centimeters of pure, powdered copper oxide is introduced, the tube being conveniently supported by a clamp in a vertical position. About .5 gram of the fertilizer is carefully introduced into the tube, and, by means of a long, stout, clean wire, bent like a corkscrew at the end, is thoroughly stirred into the copper oxide below, to a distance of about one-half the depth of the copper oxide. A little more copper oxide (about 2½ centimeters) is added, without withdrawing the wire, and the top layers of the lower stratum are mixed upwards into this. Once more a similar quantity of copper oxide is added, and the screw part of the wire thoroughly freed from any traces of the fertilizer by twisting up through this.

The tube is then filled to within 12 centimeters of the top with granular copper oxide, and, lastly, a tolerably tight-fitting roll of bright copper gauze, 7 centimeters long, is introduced. The tube is then removed from the clamp, and, while held in a horizontal position by the thumb and forefinger of both hands, it is gently tapped upon the bench. In this way the contents are made to settle down, so as to leave a narrow channel, or air space, all along the top. The tube is then placed into the combustion furnace.

A well fitting cork with a bent delivery tube is inserted, and that portion of the tube containing the granular copper oxide is carefully heated to dull redness. As soon as the tube is visibly red hot, the most forward portions of the

sodium bicarbonate are heated so as to sweep out the air from the tube by means of the CO_2 thus generated. Not more than about a little over one-third of the carbonate should be thus used at this stage.

As soon as the heating of the carbonate is commenced, the delivery tube is attached, by means of a rubber connection, to the lower branch tube of a Schiff's burette, as shown in Fig. 33. At the bottom of the burette, which is also known as a *nitrometer*, there is previously introduced a small quantity of mercury, sufficient to reach about ½ inch above the junction of the branch tube, and a strong solution of caustic potash (1 part of solid KOH in 2 parts of water) is poured into the movable reservoir *a*. The stop-cock *b* is then opened, and the burette filled with potash solution by raising the reservoir, after which the stop-cock is again closed, and the reservoir

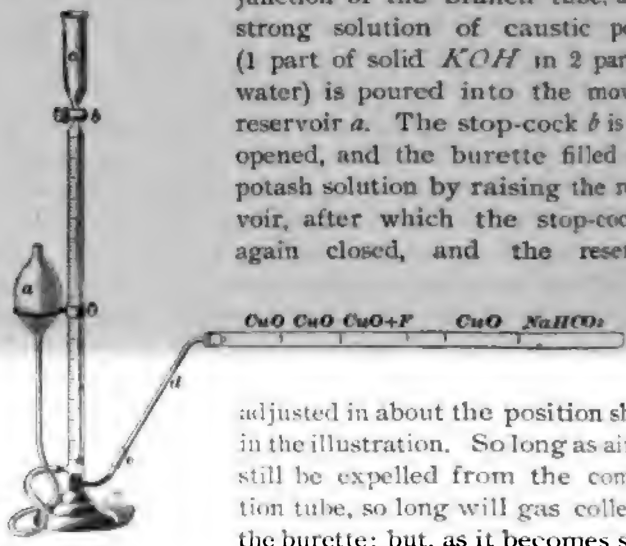


FIG. 33.

adjusted in about the position shown in the illustration. So long as air will still be expelled from the combustion tube, so long will gas collect in the burette; but, as it becomes swept out by the carbon dioxide, the ascending bubbles become smaller and smaller, until at last they are practically entirely absorbed by the potash solution. When this point is reached, the air that has collected is expelled by again cautiously raising the reservoir *a* and opening the stop-cock *b*, and the heating of the combustion tube extended first to the roll of copper gauze, and then gradually along the tube toward the mixture of copper oxide and the fertilizer.

The nitrogen that is evolved, together with the carbon

dioxide now filling the air space of the tube, passes up into the burette, and the carbon dioxide being absorbed by the potash, the nitrogen alone collects. When the evolution of nitrogen is completed, the remainder of the sodium bicarbonate is heated, whereby a fresh supply of carbon dioxide is generated, which drives out the remainder of the nitrogen now filling the tubes. This is continued until the bubbles, which enter the burette through the mercury, are absorbed as before by the potash solution.

In order, however, to make quite sure that the carbon dioxide is completely removed, the cup *c* is filled with fresh potash solution, which is slowly admitted into the burette by cautiously opening the stop-cock. When the operation is completed, the delivery tube *d* is withdrawn from the rubber connector *e*, which is then closed with a pinch cock. The reservoir is raised until the surface of the liquid it contains is level with that in the burette, in which position the apparatus is left for about 15 minutes, to insure perfect absorption of any traces of carbon dioxide that may be present. The levels are then exactly adjusted, and the volume of the nitrogen read off upon the graduated tube.

The atmospheric temperature and pressure are noted, and the volume of gas reduced to normal temperature and pressure by formula **4** (see Art. **21**). As the tension of aqueous vapor exerted by such a strong solution of potash as is here used is considerably less than that of water alone, it is usual to give to p in formula **4** the value of half the tension of vapor of water, taken from Table 1.

Since 1 cubic centimeter of nitrogen, under normal conditions, weighs 1.254 milligrams, the weight in milligrams of nitrogen contained in that quantity of fertilizer employed for the analysis is obtained by multiplying the corrected volume, in cubic centimeters, by 1.254.

Thus, suppose the corrected volume of nitrogen = 50 cubic centimeters; then, the weight of nitrogen would be $50 \times 1.254 = 62.70$, from which the percentage may be readily obtained in the usual way.

128. Soda-Lime Process.—This method is based on the fact that many substances containing nitrogen, when strongly heated with soda lime, give up their nitrogen in combination with hydrogen as ammonia. By estimating the ammonia so evolved, the weight of nitrogen can be determined.

The fertilizer is mixed with dry granulated soda lime in a combustion tube closed at one end and containing a short layer of dry oxalic acid at its closed end, in order to furnish a stream of hydrogen wherewith to sweep out the ammonia at the end of the process. The evolved ammonia is absorbed in dilute acid contained in a Will and Varrentrap's bulb tube, which is attached to the combustion tube by means of a cork. The ammonia may be estimated either gravimetrically, by precipitation as ammonium platinum chloride, in which case the gas is absorbed in dilute hydrochloric acid (1 volume HCl to 4 volumes H_2O), and the estimation carried out as described in Arts. **64** and **65**, *Quantitative Analysis*, Part 1, or it may be determined volumetrically by absorbing it in standard sulphuric acid, and titrating it with normal alkali as described in Art. **90**, *Quantitative Analysis*, Part 1. The volumetric determination is the more rapid of the two, and hence mostly used.

Into a dry combustion tube, from 40 to 45 centimeters long, is introduced a quantity of oxalic acid, previously rendered anhydrous by being heated in an air bath, sufficient to occupy about 5 centimeters. Upon this is added about the same quantity of dry, granular soda lime that has recently been moderately heated in a porcelain dish.

A quantity of soda lime, sufficient to occupy about 10 centimeters of the tube, is powdered in a dry porcelain mortar, and by means of a small spatula a weighed quantity of the fertilizer is thoroughly mixed with it. The mixture is then transferred to a sheet of clean paper and carefully poured into the tube. The mortar is then rinsed out with a little more powdered soda lime, which is also transferred to the tube. The tube will now be rather more than half full. Granular soda lime is added until it reaches to within about 5 centimeters of the mouth, and a plug of asbestos (previously

heated to redness) is inserted to keep the materials in position. The tube is then taped lengthwise on the table, in order to create a free air passage along the top of the materials, and is then laid in the furnace.

A measured volume of normal sulphuric acid, 15 to 25 cubic centimeters, depending on the capacity of the bulbs, is introduced into a Will and Varrentrap's bulb tube, shown in Fig. 34, which is then connected to the tube by a tight-fitting cork. The portion of the tube extending back from the asbestos plug, containing soda lime only, is first heated to a low redness, after which

FIG. 34.

the heating is gradually extended along until the whole of the mixture of soda lime with the fertilizer has become heated. As the heat approaches the end of the tube, a little care must be taken that the oxalic acid is not decomposed before its time. The column of pure soda lime that separates the mixture should serve to protect the acid, but additional precaution may be taken of inserting in the furnace a small screen, made of asbestos cardboard, before beginning the operation.

As soon as the evolution of ammonia is complete, the heating is extended to the oxalic acid, which is decomposed in the presence of excess of alkali with evolution of hydrogen:

$$Na_2C_2O_4 + 2NaHO = 2Na_2CO_3 + H_2$$

In this way, the ammonia still filling the tube is driven out into the acid in the bulbs. The bulbs are then disconnected and the contents transferred to a beaker, the bulbs being thoroughly rinsed out with water. The excess of sulphuric acid present is titrated with normal sodium hydrate, according to the method described in Art. **90**, *Quantitative Analysis*, Part 1.

The process should only be used for the determination of ammonia in the absence of nitrates.

129. Kjeldahl's Methods.—The most popular, and doubtless the most accurate, methods for the determination of nitrogen are those originated by the Swedish chemist *Kjeldahl*. Two of his methods, as recommended by the Association of Official Agricultural Chemists, are here given; one is for the determination of nitrogen in the absence of nitrates, and the other for that in the presence of nitrates.

The apparatus needed for these determinations consists of the following: (1) Kjeldahl's digestion flasks. These are pear-shaped, round-bottom flasks, made of hard, moderately thick, well annealed glass, having a total capacity of about 250 cubic centimeters. They are 22 centimeters long, and have a maximum diameter of 6 centimeters, tapering gradually to a long neck, which is 2 centimeters in diameter at the narrowest part, and flared a little at the edge. (2) Distillation flask and apparatus similar to that shown in Fig. 14, *Quantitative Analysis*, Part 1.

The reagents required are the following: (1) Standard sulphuric acid of known strength; half-normal acid is usually recommended. (2) Standard alkali solution, the strength of which should be relative to that of the sulphuric acid. (3) Ordinary sulphuric acid of Sp. Gr. 1.84; it must be chemically pure and especially free from nitrates and ammonium sulphate. (4) Metallic mercury or mercuric oxide. (5) Potassium permanganate which is used in a finely pulverized state. (6) Granulated zinc, pumice stone, or zinc dust; one of these reagents is added to the contents of the distillation flask, when found necessary, in order to prevent bumping. When zinc dust is used, .5 gram will usually be sufficient. (7) Potassium-sulphide solution, prepared by dissolving 40 grams of potassium sulphide in 1,000 cubic centimeters of water. (8) Sodium-hydrate solution; a saturated solution of chemically pure sodium hydrate. (9) Sodium thiosulphate. (10) Commercial salicylic acid. (11) A cochineal solution, prepared by digesting and frequently agitating 3 grams of pulverized cochineal in a mixture of 50 cubic centimeters of strong alcohol and 200 cubic centimeters of distilled water for a day or two at ordinary

temperature, is used, after being filtered, as an indicator. This solution has a reddish or orange-yellow color, and turns violet-red on the addition of an alkali.

130. Determination in the Absence of Nitrates.—From .7 to 3.5 grams of the substance to be analyzed, according to its proportion of nitrogen, are brought into a digestion flask with about .7 gram of mercuric oxide, or its equivalent in metallic mercury, and 20 cubic centimeters of sulphuric acid. The flask is placed in an inclined position and heated below the boiling point of the acid from 5 to 15 minutes, or until frothing has ceased. If the mixture froths badly, a small piece of paraffin may be added to prevent it. The heat is then raised until the acid boils vigorously. No further attention is required until the contents of the flask have become a clear liquid, which is colorless, or, at most, has a pale straw color. The flask is then removed from the flame, held upright, and, while still hot, potassium permanganate dropped in carefully and in small quantities at a time, until, after shaking, the liquid remains of a green or purple color.

After cooling, the contents of the flask are transferred to the distilling flask with about 200 cubic centimeters of water, a few pieces of pumice stone or granulated zinc, or .5 gram of zinc dust when found necessary to keep the contents of the flask from bumping, and 25 cubic centimeters of potassium-sulphide solution are added, with shaking. Next add 50 cubic centimeters of the soda solution, or sufficient to make the reaction strongly alkaline, pouring it down the sides of the flask, so that it does not mix at once with the acid solution. Connect the flask with the condenser, mix the contents by shaking, and distil until all ammonia has passed over into the standard acid. The first 150 cubic centimeters will generally contain all the ammonia. This operation usually requires from 40 minutes to $1\frac{1}{2}$ hours. The distillate is then titrated with the standard alkali, using the cochineal solution as an indicator, as described in Art. **90,** *Quantitative Analysis*, Part 1.

The use of mercuric oxide in this operation greatly

shortens the time necessary for digestion, which is rarely over 1½ hours in case of substances most difficult to oxidize, and is usually less than 1 hour. In most instances, the use of potassium permanganate is unnecessary, but it is believed that in some cases it is required to complete oxidation, and, in view of this uncertainty, it is always used.

131. Kjeldahl's Method Modified to Include the Nitrogen of Nitrates.—Place from .7 to 3.5 grams of the fertilizer to be analyzed into a Kjeldahl digestion flask, add 30 cubic centimeters of sulphuric acid containing 1 gram of salicylic acid, and shake until thoroughly mixed, then add 5 grams of crystallized sodium thiosulphate, or add to the substance 30 cubic centimeters of sulphuric acid containing 2 grams of salicylic acid, then add 2 grams of zinc dust, shaking the contents of the flask at the same time. Finally, place the flask on the stand for holding the digestion flasks, where it is heated over a low flame until all danger from frothing has passed. The heat is then raised until the acid boils vigorously, and the boiling continued until white fumes no longer escape from the flask. This requires about 5 to 10 minutes. Add approximately .7 gram of mercuric oxide, or its equivalent in metallic mercury, and continue the boiling until the liquid in the flask is colorless, or nearly so. In case the contents of the flask are likely to become solid before this point is reached, add 10 cubic centimeters more of sulphuric acid. Complete the oxidation with a little potassium permanganate, as before, and proceed with the distillation and titration as described in the preceding article.

DETERMINATION OF POTASH.

132. It is sometimes desirable to determine the potash in fertilizers, so the following method for different kinds of fertilizers is recommended by the Association of Official Agricultural Chemists:

133. Reagents Required in Potash Determination. 1. *Ammonium-chloride solution* is prepared by dissolving

100 grams of ammonium chloride in 500 cubic centimeters of water; to this, 5 to 10 grams of pulverized potassium platinic chloride are added, and the whole shaken at intervals for 6 or 8 hours. The mixture is allowed to settle overnight and filtered, and the residue is ready for the preparation of a fresh supply.

2. *Platinum Solution.*—The platinum solution used should contain 2.1 grams H_2PtCl_6 in every 10 cubic centimeters.

134. Methods of Dissolving the Fertilizer.—The following methods have to be employed according to the nature of the fertilizer under analysis:

(*a*) *With Potash Salts and Mixed Fertilizers.*—Boil 10 grams of the salt with 300 cubic centimeters of water 30 minutes. In the case of mixed fertilizers, add to the hot solution a slight excess of ammonia, and then sufficient powdered-ammonium oxalate to precipitate all the lime present. Cool, dilute to 500 cubic centimeters, mix and pass through a filter. In case of *muriate* and *sulphate of potash*, *sulphate of potash* and *magnesium*, and *kainite*, dissolve and dilute to 500 cubic centimeters without the addition of ammonia and ammonium oxalate.

(*b*) *With Organic Compounds.*—When it is desired to determine the total amount of potash in organic substances, such as cottonseed meal, tobacco stems, etc., saturate 10 grams with strong sulphuric acid, and ignite in a muffle at a low red heat, to destroy organic matter. Add a little strong hydrochloric acid, warm slightly, in order to loosen the mass from the dish, and proceed as directed in Art. **135** under *a*.

135. Determination of Potash.—(*a*) *In mixed fertilizers*, evaporate 50 cubic centimeters of the solution, corresponding to 1 gram of the sample, nearly to dryness; add 1 cubic centimeter of dilute sulphuric acid (1 part H_2SO_4 and 1 part H_2O), evaporate to dryness, and ignite to whiteness. As all the potash is in the form of sulphate, no loss need be apprehended by volatilization of potash, and a full red heat must be maintained until the residue is perfectly white. Dissolve the residue in hot water, add a few drops of

hydrochloric acid and platinum solution in excess. Evaporate on the water bath to a thick paste, and treat the residue with 80-per-cent. alcohol, Sp. Gr. .8645. Wash the precipitate thoroughly with 80-per-cent. alcohol, both by decantation and on the filter, continuing the washing after the filtrate is colorless. Wash finally with 10 cubic centimeters of the ammonium-chloride solution mentioned in Art. **133**, 1, to remove impurities from the precipitate, and repeat this washing 5 or 6 times. Wash again thoroughly with 80-per-cent. alcohol, and dry the precipitate for 30 minutes at 100°.

(*b*) *Muriate of Potash.*—Dilute 25 cubic centimeters of the solution prepared according to the description under (*a*), Art. **134**, with 25 cubic centimeters of water, acidify with a few drops of hydrochloric acid, add 10 cubic centimeters of platinum solution, and evaporate to a thick paste. Treat the residue exactly as described under (*a*).

(*c*) *Sulphate of Potash, Sulphate of Potash and Magnesia, and Kainite.*—Dilute 25 cubic centimeters of the solution, prepared according to (*a*), Art. **134**, with 25 cubic centimeters of water, acidify with a few drops of hydrochloric acid, and add 15 cubic centimeters of platinum solution. Evaporate the mixture, and proceed as directed under (*a*), except that 25-cubic-centimeter portions of ammonium-chloride solution should be used for washing.

136. Factors.—For the conversion of potassium platinichloride to KCl, use the factor .3069; to K_2SO_4 .3587; and to K_2O .1939.

ANALYSIS OF BLEACHING POWDER.

PRELIMINARY REMARKS.

137. Bleaching powder, or chloride of lime, finds wide employment in various branches of manufacture; it is formed by the action of chlorine on calcium hydrate. The relation of its constituents in the freshly prepared substance is represented by the formula $Ca_3H_6O_6Cl_4$. When allowed to stand

in contact with air and light, chloride of lime suffers decomposition, and, after treatment with water, the calcium chloride is found to have increased in quantity, while the hypochlorite has suffered a corresponding diminution. When exposed to moist air containing carbonic acid, bleaching powder is decomposed, hypochlorous acid is evolved, and calcium carbonate formed. When, therefore, chloride of lime is used as a disinfectant, the active agent in ordinary circumstances is hypochlorous acid, and not free chlorine. At a moderate temperature (50°), dry chloride of lime is converted into calcium chlorate, and the mass becomes pasty from the separation of water:

$$3Ca_3H_4O_4Cl_4 = 5CaCl_2 + Ca(ClO_3)_2 + 3Ca(OH)_2 + 6H_2O$$

This change proceeds at a diminished rate even in direct sunlight. Chloride of lime is decomposed by water, calcium hydrate separates out, and calcium chloride and hypochlorite pass into solution:

$$Ca_3H_4O_4Cl_4 = Ca(OH)_2 + CaCl_2 + Ca(ClO)_2 + 2H_2O$$

It is very probable that the hypochlorite thus formed is only produced by the action of water, and does not exist preformed in the bleaching powder.

Since the value of commercial bleaching powder depends entirely on the amount of hypochlorous acid that it can produce, and since the circumstances of heat, moisture, and exposure to air and light exercise such an important influence upon the proper production and stability of the bleaching powder, it is evident that, as manufactured and stored, it must vary very considerably in quality. The most concentrated preparation that can be obtained by saturating calcium hydrate with chlorine, contains 38.5 per cent. of available chlorine, but the great bulk of the substances found in commerce rarely contains more than from 32 to 37 per cent., of which 1 or 2 per cent. is without bleaching power, being present in the form of calcium chlorate. In badly made bleaching powder, the amount of chlorate present is occasionally as low as 8 to 10 per cent. of available chlorine—nearly one-fourth the amount that ought to be present in

the product. Many methods have been proposed to estimate the available chlorine present in bleaching powder, the majority being based on the oxidizing effect of the hypochlorites, but a great number are inaccurate, in that they do not take cognizance of the presence of this admixed chlorate, which, under the circumstances of the valuation processes, reacts like chlorine, although it has no bleaching effect.

DETERMINATION OF AVAILABLE CHLORINE.

138. Penot's Method.—This process is based on the conversion of an alkaline arsenite, by the chloride-of-lime solution, into an arseniate:

$$As_2O_3 + Ca(ClO)_2 = As_2O_5 + CaCl_2$$

The final point of the reaction is determined by means of potassium iodide and starch; so long as any hypochlorite remains undecomposed, a drop of the solution brought into contact with potassium iodide and starch renders that mixture blue. This mixture of iodine and starch is conveniently employed in the form of test paper.

139. Preparation of Test Paper.—Three grams of potato or wheat starch are rubbed into a thin cream with 50 or 60 cubic centimeters of warm water. This mixture is poured into 200 cubic centimeters of water, and the liquid heated, under constant stirring, until it boils; 1 gram of potassium iodide and 1 gram of pure carbonate of soda, dissolved in a little water, are added, and the mixture diluted to 500 cubic centimeters. A number of strips of Swedish filter paper are moistened, and, when dry, are ready for use. They should be preserved in a wide-mouthed stoppered bottle.

140. Preparation of Standard Arsenious Acid.—To prepare the arsenious-acid solution, powder a quantity of pure, white arsenic As_2O_3, and weigh off exactly 4.95 grams into a liter flask; to this add from 25 to 30 grams of pure, crystallized, sodium carbonate and 200 cubic centimeters of

water. Boil the solution gently, and shake continually until all is dissolved; cool and dilute up to the liter mark; 1 cubic centimeter of this solution corresponds to .00355 gram of available chlorine, as may be seen from the following:

$$As_2O_3 + Ca(ClO)_2 = As_2O_5 + CaCl_2$$

1 molecule of As_2O_3 can take up 2 atoms of oxygen to form As_2O_5, which are equivalent to 4 atoms of chlorine.

Molecular weight of As_2O_3 = 198.
Molecular weight of Cl_4 = 142.

Since 1 cubic centimeter of the arsenious solution contains

$$.00495 \text{ gram } As_2O_3 = \frac{4.950 \text{ grams taken}}{1{,}000 \text{ c. c. in 1 liter}};$$

then, $198 : 142 = .00495 : .00355.$

Since it is difficult to weigh out exactly the required quantity of white arsenic, it is preferable to take a round number, about 5 grams, and dilute accordingly. For example, 5.016 grams of white arsenic were weighed out into the liter flask, 30 grams of sodium carbonate and 200 cubic centimeters of water added; after complete solution and cooling, the liquid was diluted to 1 liter and 13.33 cubic centimeters of water were added by means of a burette, since,

$$4.95 : 1{,}000 = 5.016 : 1{,}013.33.$$

The solution in the flask is well shaken, and decanted off into a number of small, well stoppered bottles; this precaution diminishes the liability of the solution to change on exposure to the air.

141. Analysis.—Weigh out 10 grams of the bleaching powder, transfer to a mortar, add 50 or 60 cubic centimeters of water, and rub to a thin cream. Allow the heavier particles to settle, decant the turbid supernatant liquid, add more water, rub up again, and continue thus until all the powder has been transferred to a liter flask. Fill the flask up to the mark and shake well. Transfer 50 cubic centimeters of this solution, by means of a pipette, to a beaker, and add the arsenious solution, from a burette, with constant stirring. The end of the reaction is determined by means

of starch and potassium iodide, used as an outside indicator. After each addition of the arsenious solution, the mixture is stirred, and a drop is removed upon a glass rod, and brought into contact with a piece of the filter paper, prepared according to the directions given in Art. **139.** So long as undecomposed bleaching powder is present, the liquid will cause a blue stain upon the paper. The arsenious solution is cautiously added, until a drop of the liquid brought into contact with the paper gives no blue stain. There is no difficulty in observing the final point; the gradual increasing faintness in the blue color of the drops indicates with great accuracy the progress of the reaction. In making a second reaction, care must be taken to shake the contents of the liter flask, before withdrawing the solution; if this precaution is neglected, the second determination will give a much lower result—a difference of 2 or 3 cubic centimeters being not infrequently obtained in testing the clear and the turbid liquids.

For example, 10.99 grams of bleaching powder were treated as described, and diluted to 1 liter; 50 cubic centimeters of the turbid solution required 48.1 cubic centimeters of the arsenious solution to complete the reaction. Since 1 cubic centimeter of this solution is equivalent to .00355 of chlorine, this would correspond to $48.1 \times .00355 = .1707$ gram in the 50 cubic centimeters of solution. But 50 cubic centimeters contain .5495 gram of the bleaching powder, hence, the substance contains $\frac{.1707 \times 100}{.5495} = 31.06$ per cent. of available chlorine.

142. Iron Method.—Weigh out 10 grams of bleaching powder, place in a mortar, add about 50 cubic centimeters of water, rub to a cream; allow the coarser particles to subside, pour off the turbid, supernatant liquid into a liter flask, add more water, and rub again, and continue until the whole lot of the bleaching powder has been transferred to the flask, fill up to the mark, shake well, and remove 50 cubic centimeters, by means of a pipette, to a beaker for analysis.

Weigh out, in the meantime, .325 gram of piano wire, which will contain .324 gram of *Fe*, and dissolve it in 2 cubic

centimeters of concentrate sulphuric acid, and diluted with 10 cubic centimeters of water. Cool, fill the flask with cold water, and pour into a large beaker. Now add the 50 cubic centimeters of the turbid bleaching powder solution, pouring it in slowly and stirring constantly. Dilute the whole to about 500 cubic centimeters. Then, by means of a standardized solution of potassium permanganate, prepared as described in Art. **94**, *Quantitative Analysis*, Part 1, determine the iron still remaining in the ferrous condition.

The reaction is

$$4FeSO_4 + Ca(ClO)_2 + 2H_2SO_4 = 2Fe_2(SO_4)_3 + CaCl_2 + 2H_2O$$

from which is seen that 56 parts of Fe are equivalent to 35.5 parts of Cl.

For an example, assume that 1 cubic centimeter of the potassium-permanganate solution was equivalent to .003 gram Fe, and that 23.8 cubic centimeters of that solution were required to oxidize the ferrous iron not acted on by the bleaching powder used, in an amount equivalent to .5 gram; 23.8 cubic centimeters of permanganate correspond to $23.8 \times .003$, or .0714 gram of iron remaining unoxidized. Then, .324 (Fe taken) $-$ .0714 (Fe unoxidized) $=$ .2526 gram Fe oxidized by bleaching powder. Since 56 parts Fe correspond to 35.5 parts Cl, we have the proportion: $56 : 35.5 = .2526 : x$, when $x = .1601$ gram available Cl. .5 gram bleaching powder contains .1601 gram available chlorine, therefore 1 gram contains .3202 gram, or 32.02 per cent. available chlorine.

ANALYSIS OF SOAP.

PRELIMINARY REMARKS.

143. Soaps are mainly alkali salts of fatty acids; in fact, sodium and potassium salts. Soda soaps are hard and come into the market under the name of *compact*, *cut*, or *filled* soaps. Potash soaps are soft, and are known as *soft soaps*. Lately, however, hard potash soaps have appeared. For

analytical purposes, soap may be classified as follows: *Toilet soaps*, the best grades of which are free from impurities and free alkali. *Laundry soaps*, containing generally an excess of alkalies, in the form of either sodium silicate, sodium carbonate, or free alkali, and rosin. *Commercial soaps*, the great variety of soaps used in the arts and industries; this class may be subdivided into (*a*) *soft soaps* in which potash is the base, and (*b*) *hydrated soaps*, in which soda represents the base, being formed by caustic soda and palmnut oil or cocoanut oil. *Medicated soaps*, containing medicinal agents, such as carbolic acid, sulphur, tar, etc.

144. The complete analysis of a soap frequently presents considerable difficulty, since many adulterants may be used in the cheaper grades and many substances not adulterants, the use of which is permitted as colorants and perfume. It has been stated that besides the alkali and fatty acids and water requisite for the formation of a soap, the following substances have been found in the different varieties, namely, ocher, ultramarine, sodium aluminate, borax, resin, vermilion, arsenite of copper, alcohol, sugar, vaseline, camphor, gelatine, petroleum, naphthalene, carbolic acid, tar, glycerine, bran, starch, etc.

145. Sampling of Soap.—In analyzing soaps, care must be taken to obtain a fairly representative sample. In the case of hard soap, this is best effected by cutting a transverse slice from the middle of the bar or cake. A cylinder withdrawn from a cake by means of a cork borer or cheese sampler, also affords a fairly good sample. In many cases, it is preferable to reduce the soap to thin slices or shavings which should be thoroughly mixed and preserved in a well stoppered bottle.

DETERMINATION OF WATER.

146. The determination of the proportion of water in soap is important, and requires considerable care to insure accurate results. If the soap is solid, a fairly representative sample should be reduced to fine shavings or scraping with

a knife. A known weight is then exposed for some time to a temperature of 40° to 50°, the heat being gradually raised to 100°, and continued at that temperature as long as loss in weight is observed. The soap should not be allowed to melt.

A more rapid method that is also applicable in cases of soft soap, consists in placing from 5 to 10 grams of the sample, finely divided in the case of hard soap, into a large porcelain crucible, set in a sand bath that is heated by a small Bunsen flame. The soap is continually stirred with a glass rod (weighed with the crucible) having a roughed and jagged end, a peculiarity that greatly facilitates the stirring and breaking up of the lumps of soap formed toward the end of the operation. The operation is usually complete in 20 to 30 minutes, and is known to be at an end when a piece of plate glass placed over the crucible (the flame being removed) is no longer bedewed with moisture. Care is required, however, to prevent burning of the soap, but the odor thus developed is so characteristic that the manipulation is easily controlled.

The proportion of water in soap varies greatly; in so called dry soaps, it rarely exceeds 16 to 20 per cent., while in inferior soaps, made from cocoanut oil, it sometimes reaches 70 to 80 per cent.

DETERMINATION OF UNSAPONIFIED MATTER.

147. For the determination of unsaponified matter, the soap that has been dried by one of the processes described in the preceding article is extracted in an extraction apparatus, similar to that described in the analysis of milk (see Art. **90**) with petroleum ether, which, for that purpose, should boil below 80°, and leave no residue on evaporation. After the extraction is complete, the petroleum ether is distilled off, the residue dried at 100°, and weighed.

In a boiled, well made soap, there should be no unsaponified matter, unless the same has been added subsequently. In addition to unsaponified fats, foreign matters are sometimes found in the petroleum-ether extract, such as soft paraffin (so called mineral soap stock), waxes, phenol, etc.

DETERMINATION OF TOTAL ALKALI AND FATTY ACIDS.

148. The portion of the soap not volatile at 100° and insoluble in petroleum ether, really constitutes the *soap proper*, and is dissolved in hot water preparatory to determining the total alkali and fatty acids therein.

In analyzing soap of known origin and general composition, it is often unnecessary to go through the previous operations of drying and exhausting with petroleum ether. In such cases, it is evidently preferable to weigh out 10 grams of the original soap and at once treat it with hot water.

A pure soap dissolves completely in hot water, and no ordinary product should leave more than a slight residue. If the soap under examination is so called "scouring soap," the insoluble residue will be found to contain quantities of fine sand. The residue, if appreciable, should be washed by decantation, and eventually brought upon a filter with hot water, dried at 100°, and weighed, after which, if deemed desirable, it can be subjected to further examination.

149. To the aqueous solution is added an excess of half-normal sulphuric acid, setting free the fatty acids that rise to the surface. The beaker in which the precipitation was effected is next cooled by placing it in ice water, thus solidifying the fatty acids. When the fatty acids have solidified, it is best to decant the liquid, remelt with hot water 2 or 3 times to remove any enclosed mineral acid, cool again, filter, and wash with cold water until the washings are no longer acid, as shown by litmus.

The filtrate from the insoluble fatty acids contains the total alkali now present as sulphate, the excess of sulphuric acid and any glycerol, which may have been present in the soap if saponification has been effected in the cold. The acid liquid may further contain a small quantity of soluble fatty acids. It is first titrated with half-normal potassium hydrate, using methyl orange as an indicator. From the original amount of half-normal sulphuric acid added, and from the number of cubic centimeters of half-normal potassium hydrate required to neutralize the excess of the same,

the total alkali of the sample is calculated and reported as Na_2O.

After the liquid has been rendered neutral to methyl orange (which indicates the mineral acid), phenol-phthalein solution is added and more potassium hydrate is run in. The number of cubic centimeters of potassium hydrate required for neutralizing to phenol-phthalein solution corresponds to soluble fatty acids:

$$C_7H_{15}CO_2H + KOH = C_7H_{15}CO_2K + H_2O$$

and this is calculated to caprylic anhydride $\begin{matrix} C_7H_{15}CO \\ C_7H_{15}CO \end{matrix}\!\!>O$, in the absence of more definite knowledge as to their nature. The calculation is made by simple proportion, thus:

molecular weight of $C_7H_{15}CO_2H$: molecular weight of

$$\begin{matrix} C_7H_{15}CO \\ C_7H_{15}CO \end{matrix}\!\!>O = \text{weight of } C_7H_{15}CO_2H : x$$

In soaps containing silicates of the alkalies (a not unusual constituent), the gelatinous silicic acid that separates on the addition of sulphuric acid remains with the fatty acids on filtration. To separate the fatty acids from this, as well as other impurities, it is advisable to proceed as follows:

The funnel containing the filter, with the fatty acids, is placed in a small beaker and heated in an air bath. As the filter dries, the fatty acids pass through it and collect in the beaker below, while all impurities, silicic acid, talc, etc., remain on the filter. Of course, it is necessary to wash the filter, which remains saturated with the fatty acids, with hot alcohol or petroleum ether. The alcohol or petroleum ether is distilled off and the residue treated in the same way as described above.

DETERMINATION OF FREE ALKALI.

150. For the determination of **free alkali**, a separate portion of the sample is weighed out, and extracted in an extraction apparatus with neutral alcohol. The caustic alkali is determined in the alcoholic solution by titrating

with half-normal hydrochloric acid, using phenol-phthalein as an indicator. If, however, soap contains unsaponified fat, as is quite frequently the case when the soap is made by the so called *cold process*, this method cannot be used, since in alcoholic solution, unsaponified fat would be readily saponified by the free caustic alkali present. In such a case, the soap must be dried first in an atmosphere free from carbon dioxide at 100°, the unsaponified matter extracted with petroleum ether, and finally the soap dissolved in alcohol and the free alkali determined in the alcoholic solution, as before. The sodium carbonate, sodium silicate, borax, and everything insoluble in alcohol, remains behind in the extraction tube, and may be tried at 100°, and weighed. If considerable, it may be further treated as follows:

The residue is exhausted with boiling water, and the solution is then titrated with half-normal hydrochloric acid, using methyl orange as an indicator. The amount of acid required corresponds to carbonate, silicate, and borate, which are reported together.

DETERMINATION OF RESIN.

151. Resin is a very common constituent of soaps, the resinates of the alkalies having a similar action to soaps, and the cheapness of the material naturally suggesting a partial substitution of it for the natural fats and oils. As a qualitative test for resin, Gottlieb's method is usually employed.

152. Gottlieb's Qualitative Test for Resin.—A small quantity of the soap under examination is dissolved in water and heated to boiling. A strong solution of magnesium sulphate is added, until the fatty acids are completely precipitated. The magnesium resinates remain in solution. After boiling 2 or 3 minutes, the solution is filtered and the hot filtrate acidified with dilute sulphuric acid. In the presence of resin, the liquid becomes turbid, due to the separated resin acid. The boiling should be continued for ½ hour, to make sure that the turbidity is due to resin acids and not to volatile fatty acids.

153. Hübl's Method of Quantitative Determination of Resin.—From ½ to 1 gram of the solid mixture of fatty and resin acids, obtained as described in Art. **150**, is heated in a closed flask on the water bath with 20 cubic centimeters of alcohol to complete solution. The acids are neutralized with alkali, using phenol-phthalein as an indicator. The alcoholic-soap solution is then poured into a beaker, the flask rinsed with water, the solution diluted to about 200 cubic centimeters, and silver nitrate added to complete precipitation. The precipitate, consisting of the silver salts of resin and fatty acids, must be protected from sunlight. It is filtered off, washed thoroughly with water, dried at 100°, and extracted in an extraction apparatus with ether. The silver resinates dissolve in the ether, while the silver salts of the fatty acids remain undissolved. The ethereal solution of the resin acids should have a yellow or light-brownish color. It is filtered, if necessary, and the filtrate shaken with hydrochloric acid in a separatory funnel. The resulting ethereal solution of resin acids is filtered from the silver chloride, washed with water, and the filter and separator rinsed with ether, the ether distilled off, and the residue dried at 100°, and weighed.

As the resin is weighed in the hydrated form, its weight must be multiplied by the factor .9732 to obtain the weight of the anhydride.

154. In most analyses of soap, the following determinations are made: Water, alkali, combined as soap (as Na_2O), alkali free (as sodium hydrate), sodium carbonate, and total fatty acids as anhydrides. The composition of an ordinary yellow laundry soap is given below:

Water	19.26
Alkali combined as soap Na_2O	8.57
Alkali free as $NaOH$	0.20
Alkali as Na_2CO_3	0.20
Fatty anhydrides	52.32
Resin	19.45
Total	100.00

DETERMINATION OF SUGAR.

PRELIMINARY REMARKS.

155. The different varieties of sugar, their constitution, properties, etc. are treated under the heading "Carbohydrates" in *Organic Chemistry*, Part 4, and, in order to get a better understanding of what will be said in this section, the student is advised to study, in conjunction with these methods of analysis, the articles coming under that heading.

The investigation of sugar and saccharine products, such as beets, the juice, molasses, etc., extends as a rule to the estimation of cane sugar, invert sugar, water, alkalinity, and ash.

DETERMINATION OF CANE SUGAR.

156. Cane sugar may be determined from the specific gravity or by polarization.

157. Specific Gravity.—It is evident that an accurate estimation of sugar in solution, by means of the specific gravity of the solution, can only be executed if no other dissolved substances are present. Should other substances be in solution, they affect the specific gravity in different ways. In such solutions, only an apparent value expressed in per cent of sugar can be obtained.

The determination of specific gravity is conducted either with one of the usual forms of applicable apparatus, such as pycnometer, hydrostatic balance, densimeter, in which case the percentage of sugar corresponding to the specific gravity must be referred to in a corresponding table, or by means of an areometer specially constructed for the purpose, the saccharimeter of *Brix* or *Balling*. The object of the Balling or Brix instrument is to give in direct percentages the solid matter in solution. It is evident that for this purpose the instrument must be graduated for a particular kind of material, since 10 per cent. of sugar in solution might have

a different specific gravity from a similar quantity of another body. Instruments of this kind, graduated for pure sugar, are found very useful in technical sugar analysis. To attain greater accuracy and avoid an instrument with too long a stem, the Brix hydrometer is made in sets. A convenient arrangement is to have a set of three, graduated as follows: one from 0° to 30°, one from 25° to 50°, and one from 45° to 85°. When the percentage of solid matter dissolved is over 70, the readings of the scale are not very reliable. These instruments, similar to the Baumé hydrometer, are graduated at a fixed temperature, usually 17.5°; special tables, showing the corrections to be applied to the scale reading when made at any other temperature, are usually supplied with the instruments. A certain amount for every degree of temperature and every 5 per cent. of solids has to be subtracted or added, according as the temperature is below or above 17.5°.

158. Optical Properties of Natural Sugars.—As has been already stated in Art. **165** *et seq.*, *Physics*, and other sections, the solutions of all natural sugars have the property of deflecting the plane of polarized light, and the degree of deflection corresponds to the quantity of sugar in the solution. By measuring the amplitude of the rotation produced, the percentage of sugar in the solution can be determined. In order to secure accuracy in the determination, it is necessary that only one kind of sugar be present, or, if more than one, that the quantities of all but one be determined by other means, and the disturbances produced thereby in the total rotation be properly arranged. As a matter of fact, the process in practice is applied chiefly to cane and milk sugars, both of which occur in nature in an approximately pure state.

The instruments used for measuring the degree of deflection produced in a plane of polarized light is called a *polariscope*, *polarimeter*, or *saccharimeter*. For a theoretical discussion of the principles of polarization, and the application of these principles in the construction of saccharimeters, the

student is referred to Arts. **158** to **167,** *Physics*, and to standard works on optics and the construction of optical instruments. For the needs of the student, a description of the instruments most commonly used, and the method of using them will be sufficient.

159. The Saccharimeter.—A **saccharimeter,** or **polariscope,** for the solutions of sugar, consists essentially of a prism for polarizing the light, called, as has been previously mentioned, a **nicol,** a tube of definite length for holding the sugar solution, a second nicol made movable on its axis for adjustment to the degree of rotation, and a graduated arc for measuring it. Instead of having the second nicol movable, many instruments have an adjusting wedge of quartz of opposite polarizing power to the sugar, by means of which the displacement produced on the polarized plane is corrected. A graduated scale and vernier serve to measure the movement of the wedges and give in certain conditions the desired reading of the percentage of the sugar present. Among the large number of instruments that have been constructed for analytical purposes, only three are generally used in this country, and these will be described here.

The simplest form of a polarizing instrument consists of two nicol prisms, one of which, namely, the analyzer, is capable of rotation about its long axis. The prolongation of this axis is continuous with that of the other prism, i. e., the polarizer. The two prisms are sufficiently removed from each other to allow the interposition of the polarizing body, in a tube of definite length, the polarizing power of which is to be ascertained. See Fig. 36, *Physics*.

For purpose of description, three kinds of saccharimeter may be mentioned:

1. Instruments in which the deviation of the plane of polarization is measured by rotating the analyzer about its axis.

Instruments of this type conform to the simple type just mentioned and illustrated in *Physics*; they are under most

conditions the best as well as the cheapest. The *Laurent*, *Wilt*, *Landolt-Lippich*, etc. belong to this class.

2. Instruments in which nicols are stationary, and the direction of the plane of polarized light collected by the interposition of a wedge of a solid polarizing body.

To instruments of this type belong those of *Soleil*, *Duboscq*, *Scheibler*, and the compensating apparatus of *Schmidt and Haensch*.

3. Apparatus in which the analyzer is set in a constant angle with the polarizer, and the compensation secured by varying the length or concentration of the interposed polarizing light.

The apparatus of *Trannin* belongs to this class.

160. Appearance of Field of Vision.—Saccharimeters are also classified in respect to the appearance of the field of vision as follows:

1. Tint instruments, the field of vision of which in every position of the nicols, except that on which the plane of vibration of the polarized light is coincident with the three principal sections, is composed of two semidisks of different color.

2. Shadow instrument, where the field of vision in all, except neutral positions, is composed of two semidisks, one dark and one yellow. As the neutral position is approximated, the two disks gradually assume a light yellow color, and when neutrality is reached, they appear to be equally colored.

The *Laurent*, *Schmidt and Haensch shadow*, and *Landolt-Lippich* instruments belong to this class.

3. Striated instruments, where the field of vision is striated. The lines may be tinted as in the *Wild polaristrobometer*, or black, as in the *Duboscq* and *Trannin* instruments. The neutral position is indicated, either by the disappearance of the striæ (Wild's), or by the phenomenon of their becoming continuous (Duboscq's and Trannin's).

161. Light Employed in the Use of Polariscopes.—Polariscopes may further be distinguished as those that are

used with white light (oil lamp, etc.), and those that are used with monochromatic light (sodium flame, etc.). The Scheibler and the Schmidt and Haensch apparatus belong to the first class, while the Laurent and Landolt-Lippich apparatus belong to the second class.

Some of the instruments in common use are arranged to be used with ordinary lamps or gas light, and also with a monochromatic flame. Laurent's polarimeter is one of this kind.

162. Rotation Instrument.—This instrument has already been described as one in which the extent of deviation in the plane of polarization, caused by the intervention of an optically active substance, is measured by rotating one of the nicols about its axis, and measuring the degree of this rotation by a vernier or a graduated arc.

163. Laurent Polariscope.—A polariscope adapted by Laurent to the use of monochromatic yellow light is largely used in this country. It has the second nicol, called the *analyzer*, movable, and the degree of rotation produced is read in angular terms directly from a divided circle. The scale is graduated both in angular measurements and in per cent. of sugar for a definite degree of concentration of the solution and a definite length of the observation tube. The normal solution for this instrument contains 16.9 grams of pure sugar in 100 centimeters, and the length of the observation tube is exactly 200 millimeters. Both the angular rotation and the direct percentage of sugar can be read at the same time. The light is rendered yellow by bringing into the flames of a double Bunsen burner spoons made of platinum wire, which carry small pieces of fused sodium chloride.

164. Construction of Laurent's Polariscope.—The shadow polariscope invented by Laurent is constructed as follows: The polarizer is a special nicol that is not fixed in its position, but is so arranged that it turns about its own axis. By the device, the quantity of light passing through it can be regulated and the apparatus is thus useful with

colored solutions that are not easily cleared by any of the common bleaching agents. The greater the quantity of light admitted, however, the less delicate the reading of the shadow produced. The plane of polarized light emergent from this prism falls on a disk of glass half covered with a thin lamina of quartz that thus divides the field of vision into halves. It is this semidisk of quartz that is the distinguishing feature of the apparatus. The polarized light thus passes without hindrance the half field of vision that is covered by the glass only, but cannot pass the quartz plate unless its axis is set in a certain way. The field of vision may be thus half dark, or both halves may be equally illuminated or equally dark, according to the position of the nicol analyzer, which is freely movable about its axis and carries a vernier and reading glass over a graduated circle. The field of vision in the Laurent apparatus may have the following forms. Let the polarizer be first so adjusted that the plane of polarization of the transmitted pencil of light is parallel to the axis of the plate lying in the direction *A B*, Fig. 35. The two halves of the field of vision will then

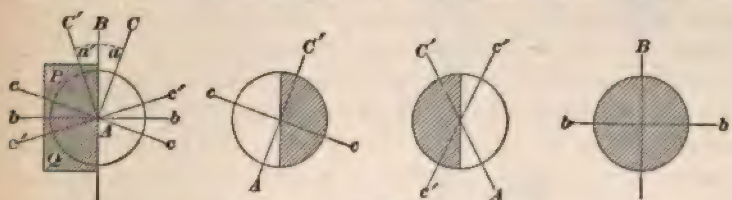


FIG. 35.

appear equally illuminated in every position of the analyzer. But, if the polarizing nicol is inclined to *A B* at an angle *a*, the plane of polarization of the rays passing through the quartz plate will undergo deviation, through an angle in the opposite direction.

It happens from this, that when in the uncovered half of the field, the plane of polarization has the direction *A C*, in the other half it will have *A C′*. When the analyzer is rotated, if its plane of polarization lie in the direction *c c*, the rays polarized parallel to *A C* will be completely extin-

guished and the corresponding half of the field will be dark. The opposite happens when the plane of polarization lies in the direction of $c' c'$. When one half of the field is thus obscured, the other half suffers only a partial diminution of the intensity of its illumination. When the middle position $b\ b$ is reached in the rotation of the analyzer, the illumination of the two halves is uniform, and this is the point at which the zero of the scale is reached. The slightest rotation of the analyzer to the right or left of this neutral point will cause a shadow to appear on one of the halves of the field, which, by an oscillatory movement of the analyzer, seems to leap from side to side. The smaller the angle a or $B\,A\,C$, the more delicate will be the shading and the more accurate the observation.

The various pieces composing the polariscope are arranged

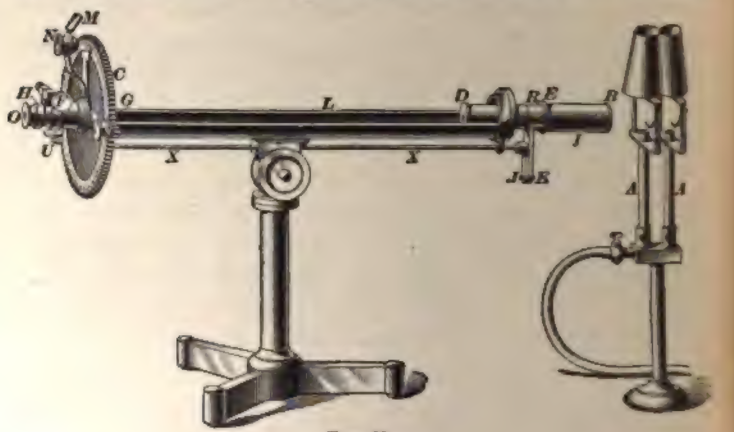


FIG. 36.

in the following positions, beginning on the right of Fig. 36, and passing to the left, where the observer is seated:

1. The lamp $A\ A$.
2. The lens B for condensing the rays and rendering them parallel.
3. The tube I, blackened inside to carry the lens.
4. A thin lamina E, cut from a crystal of potassium bichromate, serving to render the sodium light more mono-

chromatic. When the saccharine liquid under examination is colored, this crystal is removed before observation is made.

5. The polarizer *R*, which is rotatable through a small angle by the lever *K*.

6. The lever *J K*, for rotating the tube containing the polarizer. This is operated by the rod *X* extending to the left.

7. Diaphragm *D*, half covered with a lamina of quartz.

8. Trough *L* for holding the observation tube.

9. Disk *C*, carrying divided circle and sugar scale.

10. Mirror *M*, to throw the light of the lamp on the vernier of the scale.

11. Reading glass *N*, carried on the same radius as the mirror, and used to magnify and read the scale.

12. Device *F*, to regulate the zero of the instrument.

13. Tube *H*, carrying a nicol analyzer and ocular *O* for defining the field of vision. This tube is rotated by the radial arm *G*, carrying the mirror and reading glass.

165. Manipulation.—The lamp having been adjusted, the instrument, in a dark room, is so directed that the most luminous spot of the flame is in the line of vision. An observation tube filled with distilled water is placed in the trough and the zero of the vernier is placed accurately on the zero of the scale. The even tint of the field of vision is then secured by adjusting the apparatus by the device mentioned in No. 12, Art. **164.**

166. Soleil-Ventzke Polariscope.—A form of polariscope giving a colored field of vision has been constructed, that of Soleil-Ventzke being most exclusively used in this country. This instrument is very accurate and capable of rendering very good service, especially in the hands of those that have a delicate perception of color.

The general arrangement of a tint instrument, as modified by Scheibler, is shown in Fig. 37. Beginning to the right of the figure, its optical parts are as follows: *A* is a nicol, which, with the quartz plate *B*, forms the apparatus for

producing the light-rose neutral tint. The proper degree of rotation of these two parts is secured by means of the button L attached to the rod carrying the ratchet wheel as shown. The polarizing nicol at C and D is a quartz disk, one-half of which is right-handed, and the other left-handed. At G

FIG. 87.

is another quartz plate belonging to the analyzing part of the apparatus. This, together with the fixed quartz wedge F and the movable quartz wedge E, constitute the compensating apparatus of the instrument whereby the deviation produced in the plane of polarized light by the solution in the tube is restored.

Next to the compensation apparatus is the analyzing nicol, which, in this instrument, is fixed in a certain place, viz., the zero of the scale. The analyzer and the telescope for observing the field of vision are carried in the tube HJ. The movable quartz wedge has a scale that is read with a telescope K, provided with a mirror inclined at an angle of 45°, just over the scale, and serving to illuminate it. The quartz wedges are also provided with a movement by which the zero point of the scale can be adjusted. A kerosene lamp with two flat wicks is the best source of illumination, and the instrument should be used in a dark room and the light of the lamp, save that which passes through the instrument, be suppressed by a shade. The sensitive or transion tint is produced by that position of the regulating apparatus that gives a field of view of such nature that a given small

movement of the quartz compensation wedge gives the greatest contrast in color between the halves of the field of vision. For most eyes, a faint rose-purple tint, as nearly colorless as possible, possesses this quality. A slight movement of the quartz wedge by means of the screw head *M* will, with this tint, produce on one side a faint green and on the other side a pink color, which are in strong contrast. The neutral point is reached by so adjusting the quartz wedge as to give both halves of the field the same faint rose-purple tint.

167. Shadow Polariscope for Lamp Light.—Shadow polariscopes have recently come into use for saccharimetric work. They possess on the one hand, the advantages of those instruments using monochromatic light, and on the other, the ease of manipulation possessed by the tint instruments. A shadow polariscope differs from the tint instrument in dispensing with the nicol and quartz plate used to regulate the sensitive tint, and in having its polarizing nicol

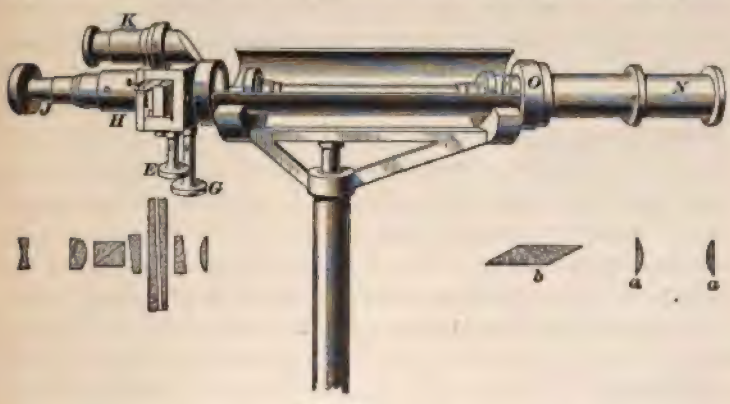


FIG. 38.

peculiarly constructed. The more improved forms of the apparatus have a double quartz-wedge compensation. The two wedges are of opposite optical properties, and serve to make the observation more accurate by mutual correction. The optical arrangement of the different parts of such an apparatus is shown in Fig. 38.

The lenses *a, a* for concentrating the rays of light and rendering them parallel are contained in the tube *N*. At *O* is placed the modified polarizing nicol *b*. The two compensating quartz wedges are moved by the milled screw heads *E, G*. The rest of the optical apparatus is arranged as described under the tint polariscope in Art. **166.**

168. When properly made, all the instruments that have been mentioned are capable of giving accurate results if used according to the minute directions supplied with each instrument. In the use of polariscopes having colored fields of vision, a delicate sense of distinguishing between related tints is necessary to do good work; color-blind persons obviously cannot use this kind of apparatus successfully; in the shadow instruments, it is only necessary to distinguish between the halves of a field of vision unequally illuminated, and reduce this inequality to zero. A neutral field is thus secured of one intensity of illumination, and of only one color, usually yellow. Such a field of vision permits of the easy discrimination between the intensity of the coloration of its two halves, and is consequently not trying to the eye of the observer, and allows great accuracy of discrimination.

The manipulation of the polariscope can only be properly learned by using it, and the student, if he follows the direction accompanying each apparatus, with a little practice will soon be able to use it efficiently.

The normal weight for most apparatus equals 26.048 grams; that is, a solution of 26.048 grams of pure cane sugar in 100 cubic centimeters in a tube 200 millimeters in length causes a rotation of 100°, or 1° corresponds with .26048 gram of sugar in 100 cubic centimeters. With the use of this normal weight and a normal tube (200 millimeters) the percentage of sugar can consequently be read off directly. When a 100-millimeter or a 400-millimeter tube is used, the degrees are to be doubled or halved.

169. Preparing Sugar Solution for Polarization. Polarization is always preceded by clarification and decolori-

zation, as a perfectly limpid liquid is of great importance to secure accurate observations. For this purpose, a solution of basic lead acetate is usually employed. This solution acts as a clarifying agent by throwing out of solution certain organic compounds and, by uniting with the organic acids in solution, forms an additional quantity of precipitate, and these precipitates act also mechanically in removing suspended matter from solution. The action of this reagent is therefore very effective for clarification purposes.

The reagent most frequently employed is of the following strength: 1½ liters of water, 464 grams of lead acetate, and 264 grams of litharge are boiled for half an hour, with frequent stirring. The solution is then allowed to cool, diluted to 2 liters, allowed to settle, and the clear solution, after being decanted, is ready for use. The specific gravity of this solution is approximately 1.267.

To 100 cubic centimeters of the sugar solution, 10 cubic centimeters of this solution are added, the precipitate is allowed to settle, and then filtered off, and the thus clarified solution is ready for polarization.

170. Errors Due to Use of Lead-Acetate Solution. In the use of lead solutions, there is some danger of errors intruding into the results of the work. These errors are due to various sources. Lead subacetate solution, when used with low-grade products, or sugar juices, or syrups from beets and canes, precipitates albuminous matter and also the organic acids present. The bulk occupied by these combined precipitates is often of considerable magnitude, so that on completing the volume in the flask, the actual sugar solution present is less than indicated. The resulting condensation tends to give too high results. With purer samples, this error is of no consequence, but especially with low-grade syrups and molasses it is a disturbing factor that must be considered.

One of the best methods of correcting it has been proposed by Scheibler, and is as follows:

To 100 cubic centimeters of a solution of a sample, 10 cubic centimeters of the lead subacetate solution are added, and

after shaking and filtering, the polarimetric reading is taken; another quantity of 100 cubic centimeters of the solution with 10 cubic centimeters of the lead solution is diluted to 220 cubic centimeters, shaken, filtered, and polarized. Double the second reading, subtract it from the first, multiply the difference by 2, and deduct the product from the first reading. The remainder is the correct polarization. Attention is here called to the fact that cane sugar is dextrorotary (+), while invert sugar is levorotary (−).

EXAMPLE.—The first polarization of a sugar solution is 30.0, the second, 14.9. What is the true percentage of sugar in the solution?

SOLUTION.— $30 - (2 \times 14.9 = 29.8) = .2$
$.2 \times 2 = .4$
and $30 - .4 = 29.6$

INVERT SUGAR.

171. Invert Sugar.—Invert sugar possesses the property of reducing Fehling's solution with separation of cuprous oxide Cu_2O. On the basis of this precipitated cuprous oxide, which is reduced to metallic copper, the amount is determined by a method that will be described later. The results obtained by polarization are influenced by the levorotary power of invert sugar. Therefore, in the presence of the latter, a different procedure, that of Clerget, is followed in the estimation of cane sugar. The description of this is given further on.

WATER.

172. Water.—The use of small, flat-bottomed porcelain or enameled sheet-iron dishes is recommended for fluid or semifluid products. Drying is done on a water bath or in an air bath at 80° to 90°, and the temperature gradually raised to 105° until constant weight is obtained.

Some chemists prefer to mix the substance (4 to 5 grams molasses, 8 to 10 grams syrup and dense juices) with 20 grams ignited quartz sand, free from dust, in a small porcelain dish. This is weighed, including a small glass stirring rod, and placed in an air bath at 100° for 15 minutes.

It is then removed from the air bath, stirred with the rod until a homogeneous mass is obtained, and again placed in the air bath and dried to constant weight.

ALKALINITY.

173. Alkalinity.—This is influenced by the presence of free alkali, lime, and free ammonia in the saccharine substance. It is estimated by titration with normal, or one-tenth normal, nitric acid, and is usually calculated into per cent. of lime. Neutral, bluish-violet litmus tincture, which is added to the liquid, is used as indicator, but in the analysis of dark-colored substances, such as molasses, the indicator is not added, but instead, after each addition of acid, the liquid is tested with a strip of bluish-violet litmus paper.

ASH.

174. Ash.—The residue left on ignition of a sugar, including the mechanically admixed impurities in the same, is called the **ash.** The residue of sugar free or freed from these impurities is called the **salts.** The latter consists mainly of alkali sulphates or chlorides and carbonates arising from salts of organic acids. Potassium predominates in these alkalies, but calcium carbonate, arising from soluble organic calcium salts, is also frequently found. These salts form a serious obstacle to the complete crystallization of the sugar, and hence cause a loss in the yield.

The complete ignition of sugar is not readily accomplished, since easily fusible alkali salts withhold small particles of carbon from combustion, and too strong a heat might cause the volatilization of alkali chlorides. The incineration is, therefore, conducted as follows: The weighed sugar is charred in a spacious platinum dish until gas is no longer evolved. The coke is then moistened with water and crushed to a paste with a pestle. After the addition of a little hot water, and heating, the mixture is filtered and the residue thoroughly washed on the filter with hot water, and

the filter and residue, after being dried, incinerated in the platinum dish. The filtrate added to this is evaporated to dryness on a water bath, moistened with ammonium carbonate, dried at 100°, and moderately ignited. The clean white residue is weighed.

In this way the *ash*, or, as it is sometimes called, the *carbonate ash*, is ascertained. If the estimation of *salts* is needed, a weighed quantity of sugar is dissolved in water, usually 25 grams of sugar in 250 cubic centimeters of water. The turbid solution is filtered, and a definite quantity of the filtrate is evaporated in a platinum dish, charred, and heated, as before.

175. Scheibler's Method for Determining Ash.—A simpler and quicker method for the determination of ash has been recommended by Scheibler, as is seen by the following: For this purpose, from 3 to 5 grams of sugar are moistened with sulphuric acid in a platinum dish. After a few minutes, the sugar blackens and is decomposed. It is then heated over a very large flame, whereby thorough charring takes place with much swelling, hissing, and gas evolution. To completely burn off the remaining coke, the dish is placed in a muffle.

The action of sulphuric acid converts the salts into sulphates, the weight of which is naturally higher than that of the salts originally present. The increase of weight equals almost exactly 10 per cent., by which the weight found must be decreased. The remainder is reported as sulphate ash.

ANALYSIS OF SUGAR BEETS.

EXTRACTION OF SUGAR.

176. Scheibler Extraction Method.—A fine paste is prepared by rasping a cross-section of the beet sample, by hand or machine. Of this paste, 35 to 40 grams are weighed out as quickly as possible on a weighed pan and placed in the

cylinder *a* of a Soxhlet extractor, shown in Fig. 39. In the wide-mouthed 100-cubic-centimeter flask *b*, with which the apparatus is provided, 75 cubic centimeters of absolute alcohol are placed. The residue on the pan is rinsed into the cylinder with absolute alcohol, and then sufficient of the latter is added to fill the cylinder almost to the top of its siphon *c*. The flask *b* is attached to the apparatus, and heated until extraction is completed. This takes, as a rule, 3 to 4 hours, in which time, the alcohol will be siphoned 80 to 90 times. The water bath, on which the bottle *b* has been resting, is withdrawn, the flask is allowed to cool, and a sufficient quantity of lead acetate, 5 to 10 cubic centimeters, is added. It is then diluted to the mark, well mixed by shaking, and polarized in a 200-millimeter tube.

The rotation observed, multiplied by .26048, gives the amount of sugar contained in the weighed paste, from which the percentage is readily obtained. If 26.048 grams of beets are used, then direct percentages of sugar are obtained.

FIG. 39.

177. Digestion Method of Rapp and Degner. — Like Scheibler's method, this one depends on an alcohol extraction, the difference being that 52.096 grams, double the normal weight that is used, are directly placed in a graduated flask of exactly 200 cubic centimeters capacity. The flask is marked down low and is provided with a widened neck, into which a condenser, about 50 centimeters in length and 10 millimeters in diameter, can be ground or securely fastened with a tight-fitting cork. Charging is done with a glass rod, and the particles adhering to this, to the pan, and to the neck of the pan, are washed in with a wash bottle containing 90 to 92 per cent. alcohol. The flask is filled to four-fifths its capacity with the same

strength alcohol. After adjusting the condenser, the flask is placed in an inclined position on a water bath already heated to boiling, and the contents of the former are kept in ebullition for 15 to 20 minutes. The sugar is thereby completely dissolved in the liquid. The flask is removed, the condenser washed with alcohol, and filled about 1 cubic centimeter above the mark, without cooling. By successive immersions into the hot water bath, to a point where ebullition begins, a thorough mixture is obtained. It is thereupon allowed to cool in the air for ½ to ¾ hour, and is finally brought to the temperature of the room by immersing in water. To the liquid, which has sunk down below the mark, 10 to 15 drops of lead acetate are added. It is then diluted to the mark with alcohol, well mixed by shaking, filtered, and polarized. The readings made with the use of a 200-millimeter tube yield direct percentages. In order to compensate, however, for the extracted pulp left in the flask, the result obtained is multiplied by .994. The true percentage is thus obtained.

178. Pellet's Method of Cold Diffusion.—The impalpable pulp of the beet having been obtained by rasping a cross-section of a beet, the contents of sugar therein is determined as follows:

A normal or double-normal quantity, i. e., 26.048 grams or 52.096 grams, of the pulp is quickly weighed, in a sugar dish shown at (*a*), Fig. 40, and washed into a sugar flask (*b*), Fig. 40, which should be graduated, as shown in the illustration, to allow for the volume of the fiber, or marc, of the beet. Since the beet pulp contains, on an average, 4 per cent. marc, the volume which is

FIG. 40

occupied thereby is assumed to be a little more than 1 cubic centimeter. Since it is advisable to have as large a volume as convenient, Pellet recommends to wash the pulp into a flask graduated at 201.35 cubic centimeters. If a 200-cubic-centimeter flask is used, the weight of the pulp should be 25.87 grams instead of 26.048 grams. After the pulp is washed into the flask, about 6 cubic centimeters of lead acetate, having a specific gravity of 30° Baumé, are added together with a little ether, to remove the foam. The flask is now gently shaken and water added to the mark, and the contents thoroughly shaken up. If the pulp has been rasped or grated finely enough, the filtration and polarization may follow immediately. The filter into which the contents of the flask are poured should be large enough to hold the whole quantity at once. If 26.048 grams have been taken, the volume diluted to 201.35 cubic centimeters, and the liquid polarized in a 200-millimeter tube, the percentage of sugar can be read off directly.

It is not necessary to heat the solution in order to insure complete diffusion, but the temperature at which the operation is conducted should be the ordinary one of the laboratory. In case the pulp is not as fine as it should be, the flask should be allowed to stand for half an hour after filling, before filtration. An insufficient amount of lead acetate may permit some rotary bodies other than sugar to pass into solution, and care should be taken always to have the proper quantity of the clarifying material added.

179. Analysis of Beet Juice.—The beet under examination is grated on an ordinary grater and about a pint of the pulp placed in the cylinder of the press shown in Fig. 41. Pressure is applied, and the thus extracted juice flows into a beaker under the spout. The juice is then poured into a tall cylindrical glass, its temperature noted, and the density observed by means of a Brix hydrometer. Of this juice, 100 cubic centimeters are then transferred by means of a pipette to a sugar flask having two graduations, one at 100 cubic centimeters and one at 110 cubic

centimeters. It is filled to the latter mark with lead acetate, and thoroughly shaken up. Clarification and decolorization are effected after a few minutes. It is then filtered and polarized in a 200-millimeter tube. The angle read off is increased by one-tenth, because of the dilution with lead acetate, and this is then multiplied by .26048. The volume percentage—the grams of sugar in 100 cubic centimeters—is thus obtained. Should the percentage by weight be desired, it is only necessary to divide the first result by the specific gravity observed by means of the hydrometer.

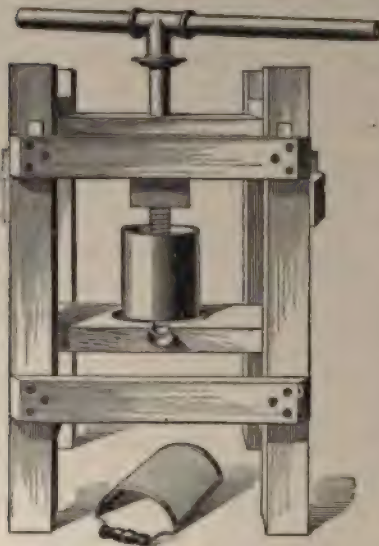


FIG. 41.

The following determinations are usually reported:

1. *Per Cent. of Total Solids in the Juice.*—This is obtained by means of the hydrometer.

2. *The Percentage of Sugar in the Juice.*—This is determined by means of the polariscope, as has been described.

3. *The Percentage of Sugar in the Beet.*—The percentage of sugar in the beet is obtained by multiplying the percentage of sugar in the juice by $\frac{95}{100}$.

4. *Percentage of Purity of a Juice.*—This term is often called the *coefficient of purity* or the *quotient of purity.* It expresses the ratio between the per cent. of total solids in the juice and the per cent. of sugar in that same juice. That is, in any particular juice, the purity expresses what proportion of the total solids is sugar. It is obtained by dividing the per cent. of sugar in the juice by the per cent. of total solids, and multiplying by 100.

The term purity is not an indication of the quality of a

juice, but the quality of the total solids in the juice; that is, it tells how many parts are sugar in every 100 parts of solids.

Below is the average of 496 samples analyzed by the writer in one season:

Per cent. solids in juice................	18.30
Per cent. sugar in juice................	15.29
Per cent. sugar in beet................	14.53
Per cent. purity......................	83.60

RAW SUGAR, FILLING MATERIAL, GREEN SYRUP, AND MOLASSES.

180. Analysis.—In the preceding articles, directions have been given for the estimation of sugar (sucrose or saccharose) by its optical properties. It has been assumed so far, that no other disturbing bodies have been present, save those that could be removed by means of clarifying agents. The case differs, however, when two or more sugars are present, each of which has a specific relation to polarized light. In such cases, some method must be used for the optical determination of sucrose that is independent of the influence of the other polarizing bodies, or else recourse must be had to other methods of analysis. The conversion of the sucrose present into invert sugar by the action of an acid or a ferment, affords an opportunity for the estimation of sucrose in mixed sugars, by purely optical methods. This process rests upon the principle that by the action of a dilute acid for a short time, or of a ferment for a long time, the cane sugar is completely changed, while other sugar present is not sensibly affected. Neither of these assumptions is rigidly correct, but each is practically applicable (see also Art. **55**, *Organic Chemistry*, Part 4).

The cane sugar by this process of hydrolysis is converted into an equal mixture of glucose and fructose, as is seen from the following equation:

$$\underset{\text{cane sugar}}{C_{12}H_{22}O_{11}} + H_2O = \underbrace{\underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}}_{\text{inverted sugar}}$$

The former, at room temperature, has the higher specific rotating power, and the deflection of the plane of polarization in a solution of inverted sugar is therefore to the left. The levorotary power of invert sugar varies with the temperature, and this arises from the optical properties of the levulose or fructose. The influence of temperature on the rotating power of other sugars is not imperceptible in all cases, but in practice is negligible.

Since the rotating power of levulose diminishes as the temperature rises, an accurate thermometric observation must accompany each polarimetric reading.

181. Qualitative Test for Invert Sugar.—Before estimating quantitatively, cane sugar in syrups, molasses, raw sugar, etc., a qualitative test for invert sugar has to be made, as the way of procedure, for the reasons given above, differs according to the presence or absence of invert sugar.

To test, qualitatively, for invert sugar, 20 grams of the substance under examination are dissolved in water, clarified by means of lead acetate, and the volume brought up to 100 cubic centimeters; 50 cubic centimeters of the clarified and filtered solution are mixed with an equal volume of Fehling's solution, placed on a piece of wire gauze on a tripod, heated to boiling, and kept boiling for 2 minutes. The formation of cuprous oxide signifies the presence of invert sugar, and the estimation of the cane sugar has to be made according to Art. **183**, while in the absence of cuprous oxide and consequently that of invert sugar, the cane-sugar determination is made according to Art. **182.**

182. Estimation of Cane Sugar in the Absence of Invert Sugar.—The normal weight, i. e., 26.048 grams, of the substance under examination, is dissolved in a flask graduated at 100 cubic centimeters, 2 to 3 cubic centimeters

of lead acetate, and 1 to 2 cubic centimeters of alum solution are added, and the volume increased to 100 cubic centimeters. The contents of the flask are thoroughly shaken, and then filtered. The filtrate is poured into a 200-millimeter tube and polarized, when the direct percentage of cane sugar can be read off.

Alumina in the form of a thin hydrate paste is frequently substituted for lead acetate, when pure sugars are used. The action of the alumina paste or cream is wholly mechanical, and, therefore, leaves the sugars in solution unchanged, carrying out only suspended matter. It is prepared by dissolving commercial aluminum chloride in 100 volumes of water and precipitating with ammonia to alkaline reaction. The precipitated aluminum hydrate is allowed to settle, the supernatant liquid is drawn off, and the precipitate washed by decantation until alkaline reaction ceases. The hydrate is suspended in pure water in proportions to produce a creamy liquid. The cream thus prepared is shaken just before using, and from 1 to 5 cubic centimeters of it, according to the degree of turbidity of the saccharine solution, are added before the volume in the flask is completed to the mark. After filling the flask to the mark, the ball of the thumb is placed over the mouth of the bottle, and the contents well shaken and allowed to stand for a few moments before filtering.

When lead acetate is used as clarifying agent it is advisable to neutralize the alkaline reaction and destroy the slight turbidity still remaining, by introducing a glass rod moistened with concentrate acetic acid.

183. Estimation of Cane Sugar in the Presence of Invert Sugar.—This process of estimation of cane sugar in the presence of invert sugar is based on the observations of Clerget and published in 1846 in the proceedings of the Society of Encouragement for National Industry.

He points out first the observations of Mitcherlich regarding the influence of temperature on the rotary power of invert sugar, and calls attention to the detailed experiments he has

made that resulted in the determination of the laws of the variation. From these studies, he was able to construct a table of correction, applicable in the analysis of all saccharine substances in which the cane sugar is polarized before and after inversion. The basis of the law rests on the observation that a solution of pure sugar, polarizing 100° on the sugar scale before inversion, will polarize 44° to the left after inversion at a temperature of 0°. The quantity of sugar operated on by Clerget amounted to 16.471 grams in 100 cubic centimeters of liquid. On the polariscope employed by him, this quantity of sugar in 100 cubic centimeters gave a reading of 100° to the right on the sugar scale when contained in a tube 200 millimeters long.

This process has been modified in many ways since; the modified detailed process, which the writer has found to give accurate result, is carried out as follows:

Half the normal quantity, i. e., 13.024 grams, of the substance under examination is dissolved with 75 cubic centimeters of water in a flask graduated at 100 cubic centimeters; 5 cubic centimeters of hydrochloric acid, Sp. Gr. 1.188, are added and the solution diluted to the mark. The mouth of the flask is then closed with the thumb and its contents shaken to mix it thoroughly. A thermometer is placed in the flask, which is set in a water bath in such a way that the water comes above the level of the liquid in the neck of the flask. The water is heated in such a manner as to bring the temperature of the contents of the flask, as determined by the thermometer, exactly to 68°, and at such a rate as to require 15 minutes to reach this result. At the end of 15 minutes, the temperature having reached 68°, the flask is removed and immediately placed in another water bath at the temperature of the room, to which temperature the contents of the flask is cooled as rapidly as possible. It is then poured into a 100-millimeter polarization tube by means of a tubulure in its center, which serves not only the purpose of filling the tube, but also to carry the thermometer afterwards, by means of which the temperature of observation

can be taken. The polarization is then observed. The result is doubled if a 200-millimeter tube is taken. After the sugar has been inverted, the liquid shows a strong levorotary power ($-I°$).

In addition to this determination, polarization as described in Art. **182** is carried out with a separate sample in the usual manner ($+P°$).

184. Calculation of the Results.—If S equals the sum of the angle of polarization before and after inversion (omitting the negative sign of the invert sugar), that is, $P° + I°$, and $t°$ equals the temperature of observation in centigrade degrees, then the cane sugar R can be calculated from the formula

$$R = \frac{100\,S}{142.66 - \frac{1}{2}\,t°}. \qquad (7.)$$

This formula is based on the fact that pure cane sugar, which, as has been already stated, rotates 100° before inversion, shows after inversion a rotation of $42.66 - \frac{t°}{2}$. Therefore, the decrease of rotation of pure sugar is $142.66 - \frac{t°}{2}$.

EXAMPLE.—Let the polarization before inversion be $+95°$, after inversion $-26°$, and the temperature 20°.

SOLUTION.—Using formula **7** and substituting the known values, we obtain:

$$R = \frac{100 \times (95 + 26)}{142.66 - 10},$$

or $$R = \frac{12{,}100}{132.66} = 91.21 \text{ per cent. of cane sugar. Ans.}$$

185. Estimation of Invert Sugar.—When the presence of invert sugar has been established by means of the qualitative test given in Art. **181**, before determining its quantity finally, an approximate quantitative test has to be made. This is done by dissolving 10 grams of the substance in water, clarifying it with an appropriate amount of lead acetate, filtering and diluting the mixture to 100 cubic centimeters. Each cubic centimeter of this solution contains

.1 gram of the original substance, and 10, 8, 6, 4, and 2 cubic centimeters of it are placed in separate test tubes, 5 cubic centimeters of Fehling's solution are added to each, and the contents are then boiled. Notice is taken of the tube whose contents are nearly decolorized. Should this be the case, for instance, with the one containing 10 cubic centimeters, there is less than 1.5 per cent. of invert sugar present, and the final determination is conducted according to the method of Herzfeld (see Art. **186**). In the other case, the method of Meissl and Hiller is employed (see Art. **188**). For the latter method, the number of cubic centimeters in that test tube which is nearly decolorized gives simultaneously the number of grams that, dissolved in 50 cubic centimeters, are used in the final determination.

Every cubic centimeter of sugar solution (10 grams in 100 cubic centimeters) corresponds to .1 gram of substance. But in the method of Meissl and Hiller, 10 times the amount of Fehling's solution (50 cubic centimeters) is used; hence, 10 times the quantity of sugar is also taken, and, consequently, every cubic centimeter of solution in the preliminary test represents 1 gram of substance in the latter determination.

Should the test, therefore, show that decolorization took place with 8 cubic centimeters, but that with 6 cubic centimeters a blue tint remained, then 6 grams dissolved in 50 cubic centimeters of water are used.

186. Herzfeld's Method of Estimating Invert Sugar.—A solution, clarified with lead acetate containing the normal weight (26.048 grams) of the substance in 100 cubic centimeters, is used. This is precipitated with sodium carbonate when any great excess of lead acetate has been used. In case precipitation with sodium carbonate is not necessary, 38.4 cubic centimeters of filtered solution, diluted to 50 cubic centimeters, which would correspond to 10 grams of the substance, are used. When, however, precipitation with sodium carbonate is necessary, 46.07 cubic centimeters

of solution, diluted to 60 cubic centimeters with concentrate sodium-carbonate solution, are withdrawn and filtered; 50 cubic centimeters of the filtrate are then employed, and these also correspond to 10 grams of the substance under examination.

These 50 cubic centimeters are placed in an Erlemeyer flask or a dish, together with 50 cubic centimeters of Fehling's solution, and heated with a large burner to boiling. That moment is accepted as the beginning of ebullition when bubbles arise from the sides as well as from the bottom of the containing vessel. The flame of the burner is then somewhat reduced and the boiling continued for exactly 2 minutes. After the expiration of 2 minutes, the vessel is removed from the flame, 100 cubic centimeters of cold water (previously boiled) are added and the contents are rapidly filtered, with the aid of a filter pump, on a weighed asbestos filter, shown in Fig. 42. The precipitate is rapidly washed, first by decantation and then on the filter, using altogether about 300 to 400 cubic centimeters of hot water; this is followed by a washing with about 20 cubic centimeters of alcohol, finally by one with ether, and then the tube is dried in an air bath at 120° to 130°.

FIG. 42.

The portion of the tube containing the cuprous oxide on the filter is next heated to a low, red heat to oxidize and destroy all organic matter, and is then reduced to metallic copper by heating slowly in a current of hydrogen. Reduction requires only moderate heat and is complete in a few minutes. It is allowed to cool in hydrogen, and the water collected in the neck is allowed to evaporate. It is then placed in a desiccator and weighed after 15 minutes. The invert sugar is gotten from the amount of reduced copper by means of Table 4.

TABLE 4.

TABLES OF HERZFELD.

Copper. Milligrams.	Invert Sugar. Per Cent.	Copper. Milligrams.	Invert Sugar. Per Cent.	Copper. Milligrams.	Invert Sugar. Per Cent.	Copper. Milligrams.	Invert Sugar. Per Cent.
50	.05	120	.40	190	.79	260	1.19
55	.07	125	.43	195	.82	265	1.21
60	.09	130	.45	200	.85	270	1.24
65	.11	135	.48	205	.88	275	1.27
70	.14	140	.51	210	.90	280	1.30
75	.16	145	.53	215	.93	285	1.33
80	.19	150	.56	220	.96	290	1.36
85	.21	155	.59	225	.99	295	1.38
90	.24	160	.62	230	1.02	300	1.41
95	.27	165	.65	235	1.05	305	1.44
100	.30	170	.68	240	1.07	310	1.47
105	.32	175	.71	245	1.10	315	1.50
110	.35	180	.74	250	1.13		
115	.38	185	.76	255	1.16		

187. The following details are yet to be considered: The asbestos must be proof against acids and alkalies, and should be previously ignited. It is then suspended in water, poured on the glass wool in the tube, and pressed with a glass rod having a flattened end, so that a thin but perfectly solid layer that filters without the use of the pump is formed. It is then washed with alcohol, dried, and weighed. During filtration, a short, thick funnel is loosely placed on the tube, but, while washing, the latter is replaced by a funnel attached tightly to the tube by means of a rubber stopper, as is shown in Fig. 42. The liquid in the tube should not be allowed to run off entirely while washing. The hydrogen used in reducing must be free from arsenic. The tube is attached to the drying bottle by a glass and rubber tube in a tight-

fitting rubber stopper, and is inclined upwards, as shown in Fig. 43. Instead of using glass wool to rest the asbestos on

FIG. 43.

in the filter tube, a perforated platinum disk is very convenient.

Instead of asbestos filter, filter paper washed with hydrofluoric acid may be used. In this case, likewise, 300 to 400 cubic centimeters of hot water are used in washing. It is then incinerated, placed in a Rose crucible, covered with the perforated lid, and reduced in hydrogen.

188. Meissl and Hiller's Method for Estimating Invert Sugar.—This method is generally used when the amount of invert sugar exceeds 1.5 per cent. The necessary quantity of substance for analysis is determined from the above mentioned experiments (see Art. **185**). In order to obtain this dissolved in 50 cubic centimeters, double the quantity is weighed out, brought into solution, and the volume made up to 100 cubic centimeters. It is clarified, filtered, and 50 cubic centimeters of the filtrate are used. With this quantity, the estimation of invert sugar is conducted in the same way as in the Herzfeld method.

TABLE 5.

MEISSL AND HILLER'S FACTORS FOR THE DETERMINATION OF MORE THAN 1.5 PER CENT. OF INVERT SUGAR.

Ratio of Cane Sugar to Invert Sugar = $R:I$.	I = 200 milligrams.	I = 175 milligrams.	I = 150 milligrams.	I = 125 milligrams.	I = 100 milligrams.	I = 75 milligrams.	I = 50 milligrams.
0:100	56.4	55.4	54.5	53.8	53.2	53.0	53.0
10:90	56.3	55.3	54.4	53.8	53.2	52.9	52.9
20:80	56.2	55.2	54.3	53.7	53.2	52.7	52.7
30:70	56.1	55.1	54.2	53.7	53.2	52.6	52.6
40:60	55.9	55.0	54.1	53.6	53.1	52.5	52.4
50:50	55.7	54.9	54.0	53.5	53.1	52.3	52.2
60:40	55.6	54.7	53.8	53.2	52.8	52.1	51.9
70:30	55.5	54.5	53.5	52.9	52.5	51.9	51.6
80:20	55.4	54.3	53.3	52.7	52.2	51.7	51.3
90:10	54.6	53.6	53.1	52.6	52.1	51.6	51.2
91:9	54.1	53.6	52.6	52.1	51.6	51.2	50.7
92:8	53.6	53.1	52.1	51.6	51.2	50.7	50.3
93:7	53.6	53.1	52.1	51.2	50.7	50.3	49.8
94:6	53.1	52.6	51.6	50.7	50.3	49.8	48.9
95:5	52.6	52.1	51.2	50.3	49.4	48.9	48.5
96:4	52.1	51.2	50.7	49.8	48.9	47.7	46.9
97:3	50.7	50.3	49.8	48.9	47.7	46.2	45.1
98:2	49.9	48.9	48.5	47.3	45.8	43.3	40.0
99:1	47.7	47.3	46.5	45.1	43.3	41.2	38.1

189. Calculating the Results Obtained by Meissl and Hiller's Method.—For the calculation of the results, the following formulas and Table 5, containing the necessary factors worked out by Meissl and Hiller, are to be used:

Let Cu = weight of copper obtained;

P = polarization of sample (obtained as described in Art. **183**);

W = weight of sample in the 50 cubic centimeters of the solution used in Meissl and Hiller's determination;

F = factor obtained from Table 5:

$\frac{Cu}{2}$ = approximate absolute weight of invert sugar = Z;

$Z \times \frac{100}{W}$ = approximate per cent. of invert sugar = y;

$\frac{100\,P}{P+y}$ = R = relative number for cane sugar;

$100 - R$ = I = relative number for invert sugar;

$$\frac{Cu\ F}{W} = \text{per cent. of invert sugar.} \qquad (8.)$$

Z indicates the vertical column, and the ratio of R to I, the horizontal column of Table 5, which are used to find the factor F for calculating copper to invert sugar.

EXAMPLE.—The polarization of a sugar is 86.4, and 3.256 grams of it (W) are equivalent to .290 gram of copper. What is the percentage of invert sugar?

SOLUTION.— $\frac{Cu}{2} = \frac{.290}{2} = .145 = Z.$

$$Z \times \frac{100}{W} = .145 \times \frac{100}{3.256} = 4.45 = y.$$

$$\frac{100\,P}{P+y} = \frac{8,640}{86.4+4.45} = 95.1 = R.$$

$$100 - R = 100 - 95.1 = 4.9 = I.$$

$$R : I = 95.1 : 4.9.$$

By consulting the table, it will be seen that the vertical column headed $I = 150$ is nearest to Z, 145, the horizontal column headed 95 : 5 is nearest to the ratio of $R \cdot I$ (95.1 : 4.9). Where these columns meet, we find the factor 51.2 which enters into the final calculation

$$\frac{Cu\,F}{W} = \frac{.29 \times 51.2}{3.256} = 4.56, \text{ the true percentage of invert sugar present. Ans.}$$

EXAMPLES FOR PRACTICE.

190. Solve the following examples:

1. A sample of raw sugar polarizes, before inversion, + 94°; after inversion, at 21° it polarizes − 23°. What is the percentage of cane sugar in the sample? Ans. 88.529 per cent.

2. Another sample polarizes, before inversion, + 97°; after inversion, − 19°; the temperature at the latter observation was 21.5°. What is the percentage of cane sugar in the sample? Ans. 87.938+ per cent.

3. A sample of molasses contains 93 per cent. of cane sugar; its analysis by Meissl and Hiller's method gave .35 gram of copper and 4.3 grams of molasses had been used in this last estimation. What is the percentage of invert sugar in the sample? Ans. 4.167 per cent.

4. A sample of raw sugar polarizes, before inversion, + 96°; after inversion, − 20° at 18°. For Meissl and Hiller's determination 4 grams were used and .36 gram of copper has been obtained. What percentage of cane sugar and invert sugar is contained in this sample?

Ans. { 86.787 per cent. cane sugar. 4.689 per cent. invert sugar.

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191. Water and Ash Determination.—Water and ash are determined in the manner previously described. Sugar, water, and ash added together and deducted from 100 yields the non-saccharine organic matter.

192. Alkalinity.—What has been stated in Art. 173 applies also in this case. When molasses is used, 15 to 20 grams are dissolved and diluted to 250 cubic centimeters; 25 to 30 cubic centimeters of this solution are placed in a graduated cylinder and 1 to 2 cubic centimeters of litmus tincture are added. If the cylinder is held horizontally over a white piece of paper, a grayish-green color is observed in the liquid when the molasses is alkaline. In this case, another portion is titrated with standard acid, as in the method already mentioned.

To distinguish whether a molasses is neutral, the contents of the cylinder are divided into two parts. To one part, 1 drop of normal acid is added; to the other, add 1 drop of normal alkali, whereupon the solutions, if originally neutral, should become either red or blue.

193. Rendement or Yield.—Rendement or yield is the number that designates how much crystallized cane sugar is capable of being obtained from a raw sugar. The customary calculation in practice fundamentally assumes 5 parts by weight; sugar is prevented from crystallizing by 1 part by weight of soluble salts. The rendement is therefore obtained by deducting 5 times the weight of salt content from the cane-sugar content. The assumption is rather an arbitrary one.

194. Preparation of Fehling's Solution.—Fehling's solution is made up in two different solutions: (*a*) 34.639 grams of crystallized copper sulphate are dissolved in 500 cubic centimeters of water; (*b*) 173 grams of Seignette salts are dissolved in 400 cubic centimeters of water; 100 cubic centimeters of sodium-hydrate solution, containing 50 grams caustic soda, are added. The solutions are kept separate, and are mixed in equal volumes prior to every experiment.

ANALYSIS OF ASPHALT AND ASPHALTIC SUBSTANCES.

195. Under this heading may be understood natural bitumens, varying in physical properties from hard, resonant, vitreous matter to soft, sticky masses. The former are known under the technical name of **asphalt,** and the latter under the name of **maltha.** With more or less mineral matter, which, likewise, can vary in physical and chemical composition, they belong to the product that, when admixed with suitable constituents and subjected to various processes, forms the basis of artificial paving. Little is known regarding the origin of these substances and the nature of their organic constituents.

A general description of analysis will be given. The analysis includes the estimation of water, substances soluble in petroleum ether, or *petrolene*, substances soluble in carbon disulphide or turpentine, called *asphaltene*, organic matter not bitumen, and mineral matter.

ANALYTICAL PROCESSES.

196. Water.—Of the substance, 2 to 5 grams are divided as finely as possible or spread over as large a layer as possible and dried over sulphuric acid in a desiccator. The substance is reweighed and the remaining results are based on anhydrous material.

197. Petrolene.—On a weighed filter are weighed 2 to 5 grams of substance. The filter must be fitted into a much larger funnel, provided with a stop-cock on its exit tube. The contents are repeatedly washed with petroleum ether every few minutes. To remove the last traces, digest for several hours. The filter and contents are dried in a steam bath and weighed. The loss in weight represents *petrolene.*

198. Asphaltene.—The filter and contents of the previous examination are replaced on the funnel and extracted in a similar manner with turpentine. After complete exhaustion, which, at times, is tedious, the contents are washed with alcohol, dried, and weighed as before. The difference represents *asphaltene soluble in turpentine.*

The process is repeated, using chloroform for extraction. The difference represents *asphaltene soluble in chloroform.*

The three fractions are summed up as *total bitumen.*

199. Mineral Matter.—The residue is ignited in a platinum dish, cooled, and weighed. In case carbonates are present, the ash must be recarbonated by ignition with ammonium carbonate.

Matter not bitumen is that which remains when the sum of the percentages of the four previous determinations are deducted from 100.

ANALYSIS OF FATS, WAXES, AND MINERAL OILS.

INTRODUCTORY.

200. Fats are mixtures of triglycerides of monobasic fatty acids. Vegetable and animal waxes are fatty-acid esters of higher fatty alcohols. Mineral waxes and mineral oils consist of hydrocarbons.

The groups named, representing different chemical constitutions, show characteristic behavior toward alkalies. Fats

are saponified on treatment with alkali into salts of fatty acids (soaps) and glycerine, both of which are soluble in water. Fats, therefore, are *completely saponifiable.* Vegetable and animal waxes yield salts of fatty acids soluble in water and insoluble in higher fatty alcohols by this treatment, and are termed *incompletely saponifiable.* Mineral waxes and oils are not changed by alkalies; they are unsaponifiable.

FATS.

GENERAL METHODS OF INVESTIGATION.

201. Although the fats represent mixtures of many triglycerides, the quantity of the same in every kind of fat is a fairly constant one. In consequence of these so called constants, slightly varying values can be determined for each fat. These would lead with certainty to the identification of the same. Of these constants, there will be described:

1. *The Saponification Number.*—This indicates how many milligrams of potassium hydrate are necessary to saponify 1 gram of fat, and is, therefore, a representation of the capacity of saturation of the fatty acid contained in the fat.

2. *Hübl's Iodine Number.*—This represents the quantity of iodine that fat is capable of absorbing, and serves as a measure for the unsaturated acid present (oleic and linoleic acids and linoleic-acid series).

3. *The Acetyl Number.*—This is a measure of the fatty oxacids and fatty alcohols present.

4. *The Acid Number.*—This expresses the number of milligrams of potassium hydrate used to neutralize the free fatty acids in 1 gram of fat. It serves, therefore, as a measure for the free acids of the fat.

SAPONIFICATION NUMBER.

202. Röttstorfer's Number.—The necessary reagents to determine the saponification number are: (*a*) About a half-normal hydrochloric-acid solution, the exact value of

which has been determined by titrating with potassium hydrate. (*b*) An alcoholic solution of potassium hydrate, prepared by dissolving in a little water 30 grams of potassium hydrate in sticks, purified by alcohol, and then diluting to 1 liter with alcohol free from fusel oil. The solution is allowed to stand for 24 hours and is then filtered into a flask. A 25-cubic-centimeter pipette, provided above with a piece of rubber tubing and a clip, is inserted into the single perforation of a tight-fitting rubber stopper. When pure alcohol is used, the solution will, at the utmost, assume a slightly pale-yellow tint on standing; otherwise, it will soon assume a brown color, and must not be employed.

To conduct the operation, 1 to 2 grams of the substance are placed in a wide-necked flask of about 150 to 200 cubic centimeters capacity. For the purpose of weighing, a small bottle with a lip is preferable. Introduce 50 to 60 drops of oil from the weighing bottle into the flask and reweigh the bottle; 25 cubic centimeters of the alcoholic-potash solution are introduced into the flask by means of the pipette before mentioned. An upright condenser is fitted into the flask and the whole heated to boiling on a water bath, and shaken from time to time. Saponification is, as a rule, complete in 15 minutes; but, with difficultly saponifiable fats, $\frac{1}{2}$ hour is occasionally required. A few drops of phenol-phthalein solution are then added and the excess of alkali titrated with the half-normal hydrochloric-acid solution.

Since the standard of the alcoholic potash alters somewhat, 25 cubic centimeters of it are titrated anew with the hydrochloric acid prior to each experiment. The same conditions as heretofore are to be observed, namely, the same period of heating on the water bath and the same degree of heat. The difference between the number of cubic centimeters of hydrochloric acid used in this and the previous titration is expressed in milligrams KOH and calculated to 1 gram fat to obtain the saponification number.

IODINE NUMBER.

203. Hübl's Iodine Number.—The determination of the iodine absorption of oils and fats is probably the most important test. Although iodine acts only slowly on fats, unsaturated fatty acids readily form chloriodine addition products on treatment with an alcoholic solution of iodine and mercuric chloride. The reagents required are as follows:

1. *Iodine Solution.*—Pure iodine to the amount of 25 grams is dissolved in 500 cubic centimeters of 95-per-cent. alcohol free from fusel oil, and 30 grams of mercuric chloride in the same volume of alcohol. The latter solution, if necessary, is filtered, and then the two solutions mixed. The mixed solution should be allowed to stand at least 12 hours before using.

2. *Decinormal Sodium-Thiosulphate Solution.*—This is prepared by dissolving 24.6 grams of chemically pure sodium thiosulphate, freshly pulverized as finely as possible and dried between filter paper, in water, and making up the solution to 1 liter.

3. *Starch Paste.*—For 10 minutes, 1 gram of starch is boiled in 200 cubic centimeters of distilled water, and cooled to room temperature.

4. *Solution of Potassium Iodide.*—Potassium iodide to the amount of 150 grams is dissolved in water, and the solution made up to 1 liter.

5. *Solution of Potassium Bichromate.*—Chemically pure potassium bichromate to the amount of 3.874 grams is dissolved in distilled water, and the volume made up to 1 liter.

204. Standardizing the Sodium-Thiosulphate Solution.—Place 20 cubic centimeters of the potassium-bichromate solution, to which has been added 10 cubic centimeters of the solution of potassium iodide, in a glass-stoppered flask. Add to this mixture 5 cubic centimeters of strong hydrochloric acid. Allow the solution of sodium thiosulphate to flow slowly into the flask from a burette until the liquid becomes nearly colorless. Add then a few drops of

starch solution, and, with constant shaking, continue to add sodium thiosulphate until the blue color just disappears. The number of cubic centimeters of thiosulphate solution used, multiplied by 5, is equivalent to 1 gram of iodine.

For example, 20 cubic centimeters of potassium-bichromate solution required 16.2 cubic centimeters of sodium thiosulphate; then $16.2 \times 5 = 81$ = number of cubic centimeters of thiosulphate solution equivalent to 1 gram of iodine. Then, 1 cubic centimeter of sodium thiosulphate = .0124 gram of iodine.

205. Actual Determination of Iodine Number. From .15 to .18 gram of drying oils, .25 to .30 gram of non-drying oils, or .8 to 1 gram of solid fats, is weighed into a glass-stoppered bottle of 300 cubic centimeters capacity. To this is added 10 cubic centimeters of chloroform, and, after solution has taken place, 30 cubic centimeters of the iodine solution are added. The flask is then set aside in a dark place and allowed to stand, with occasional shaking, for at least 3 hours.

To the contents of the flask, 100 cubic centimeters of distilled water are added, together with 20 cubic centimeters of the potassium-iodide solution. Any iodine that may be noticed on the stopper of the flask should be carefully washed back into the flask with the potassium-iodide solution. The excess of iodide is now taken up with the sodium-thiosulphate solution, which is run in gradually from a burette, with constant shaking, until the color of the solution has almost disappeared. A few drops of starch paste are then added, and the titration continued until the blue color, produced by the addition of the latter, has entirely disappeared. Toward the end of the reaction, the flask should be stoppered and violently shaken, so that any iodine remaining in solution in the chloroform may be taken up by the potassium-iodide solution in water. A sufficient quantity of sodium-thiosulphate solution should be added to prevent the reappearance of any blue color in the flask for 5 minutes.

TABLE 6.

Fats.	Iodine Number.			Saponification Number.		
	Minimum.	Maximum.	Mean.	Minimum.	Maximum.	Mean.
Olive oil	79	88	82–83	185	196	193
Sesame oil	103	112	108–109	187	192	190
Peanut oil	87.3	103	94–96	190	197	194
Cotton oil	102	112	108–109	191	198	195.5
Castor oil	82	85.9	84.5	176	183	180
Rape-seed oil	98	104	100–101	175	179	177
Linseed oil	170	183	178	187.4	195.2	192
Hemp-seed oil	140.5	157.5	150	190	193	191.5
Sunflower-seed oil	122	134	128	189	194	192
Cod-liver oil	123	166	144–148	175	194	182–187
Palm oil	51	52.4	51.5	200	202.5	201.5
Cocoanut oil	8	9.35	8.5	253	262	257
Butter fat	26	35	33	221	227	224
Tallow	35.5	44	39	193	206	197
Bone fat	46	55	49	....	....	190.9

At the time of adding the iodine solution to the oils or fats, two flasks of the same size as that used for the determination should be employed for conducting the operation described above, but without the addition of the oils or fat. In every respect, the performance of the blank experiments should be just as described. The blank determinations must be made each time the iodine solution is used; for example:

BLANK DETERMINATIONS.

(1) 30 c. c. of iodine solution required 46.4 c. c. of sodium-thiosulphate solution.

(2) 30 c. c. of iodine solution required 46.8 c. c. of sodium-thiosulphate solution.

Mean equals 46.6 c. c.

Per cent. of iodine absorbed:

Weight of oil taken	1.0479 gr.
Quantity of iodine solution used	30 c. c.
Thiosulphate equivalent to iodine used	46.6 c. c.
Thiosulphate equivalent to remaining iodine	14.7 c. c.
Thiosulphate equivalent to iodine absorbed	31.9 c. c.

Per cent. of iodine absorbed, $31.9 \times .0124 \times 100 \div 1.0479 = 37.75$, which would be the *iodine number* for the oil under examination.

Table 6 contains the iodine numbers and saponification numbers of the most important fats. The maximum and minimum values shown in the table are rarely found. Normal values are those under the heading "Mean."

ACETYL NUMBER.

206. The acetyl number of Ulzer and Benedict expresses the number of milligrams of potassium hydrate that is necessary to saponify the acetyl groups in 1 gram of acetylized fat.

To determine this, the free fatty acids must first be isolated from the fats, for which purpose 30 grams of fat are placed in a flask with 60 to 70 cubic centimeters of alcohol and 10 grams potassium hydrate, dissolved in a little water. This is boiled on a water bath with an upright condenser to complete saponification. The latter is finished when, after addition of some water and shaking, the liquid remains perfectly clear. The excess of alcohol is evaporated on the water bath. The remaining soap is dissolved in warm water and is poured into a beaker of 1,000 cubic centimeters capacity. The solution is boiled with dilute sulphuric acid until the fats are completely melted. A current of carbonic-acid gas is, at the same time, run through the solution to prevent bumping. Thereupon the acid fluid is siphoned off and the fats are again boiled with water. The acid liquor is again siphoned off, and the operation is repeated until the liquid siphoned off no longer reacts acid. The acids are filtered on a hot-water funnel through a dry filter and are

acetylized by boiling for 2 hours with an equal volume of acetic anhydride in a flask provided with an upright condenser. The contents of the flask are poured into a beaker of 1,000 cubic centimeters capacity, mixed with 500 to 600 cubic centimeters of water and boiled for ½ hour. As before, carbonic-acid gas is conducted through a tube extending nearly to the bottom of the beaker. After the expiration of the time mentioned, the water is siphoned off, and the boiling with fresh portions of water is repeated three times, whereby all acetic acid is removed. Finally, the acetylized acids are filtered in an air bath at about 80° through a dry filter. In a portion of the acetylized acids, the saponification number is determined, as has been described in the preceding articles. This gives the *acetyl saponification number*. In another portion, the *acetyl acid number* is determined as described in Art. **207**, in the method for acid number. The difference between the two gives the *acetyl number*. If a fat contains no fatty oxacids, its acetyl number will equal zero.

ACID NUMBER.

207. Determination of Acid Number.—Acidity in oil is generally due to partial decomposition of the oil with liberation of fatty acids. These latter act as corrosive agents, attacking the metal bearings of machinery, forming metallic soaps and producing gumming and thickening of the lubricant.

Properly refined mineral oils are free from acidity, but nearly all animal and vegetable oils possess it more or less. In palm oil, for instance, the free fatty acids vary from 12 to 80 per cent., and, in olive oil, from 2.2 to 25.1 per cent. of free acid (oleic) has been found.

Oleic acid cannot, of course, be present as a constituent of a pure mineral oil; still the acid test should be made, since poorly refined mineral oils are liable to contain small amounts of sulphuric acid left in the process of refining.

About 10 grams of the substance under examination are slightly heated in a flask with about 50 cubic centimeters of

pure, acid-free, 95-per-cent. alcohol, while the liquid is agitated. On cooling, phenol phthalein is added, and the solution titrated with half-normal alkali until the red color appears. The number of milligrams of potassium hydrate required, calculated to 1 gram of the substance, yields the acid number. When free fatty acids are used, the acid number is identical with the saponification number.

Frequently, the acid number of a substance is expressed in *Burstyn degrees*. These express the number of cubic centimeters of normal alkali necessary to combine with the free acids present in 100 cubic centimeters of the substance.

COLOR REACTIONS OF OILS.

208. Many fatty oils, when treated with chemical reagents, very often produce strongly colored products. To a certain extent, these color reactions are characteristic of the oils by which they are produced, and, hence, may be employed for their identification. It must be remembered, however, that the albuminous, resinous, and other foreign matters, on the presence of which the color reactions in most cases depend, are more or less completely removed or modified by the process employed for refining oil. Hence, considerable variations are observed in the behavior of different samples of oil with the same reagent, and the value of the reactions is still further reduced by the modifications produced by the presence of free fatty acids in the oils. Still less are the indications to be trusted when mixed oils are examined. Notwithstanding these drawbacks, color tests, when carefully applied, are often capable of furnishing valuable information, and sometimes render the positive identification of an oil, or its detection in a mixture, possible, when no other means are available.

The reactions with strong sulphuric and nitric acids are the most valuable; it is advisable, in employing color tests, to examine specimens of oils of known purity side by side with the sample, instead of trusting too implicitly the reactions described.

TABLE 7.

COLOR REACTIONS OF VEGETABLE OILS.

Name of Oil.	1 or 2 Drops of Strong Sulphuric Acid to 20 of Oil.	
	Before Stirring.	After Stirring.
Olive oil	Yellow, green, or pale brown.	Light brown, or olive green.
Almond oil	Colorless, or yellow.	Dark yellow, olive, or brown.
Arachis oil	Grayish yellow to orange.	Greenish, or reddish brown.
Rape-seed oil, crude	Green with brown rings	Bright green, turning brownish.
Rape-seed oil, refined	Yellow, with red or brown rings.	Brown.
Mustard oil	Dark yellow, with orange streaks.	Reddish brown.
Cottonseed oil, crude	Very bright red.	Dark red, nearly black.
Cottonseed oil, refined	Reddish brown.	Dark reddish brown.
Niger-seed oil	Yellow, with brown clot	Reddish or greenish brown.
Poppy-seed oil	Yellow spot, with orange streaks or rings.	Olive or reddish brown.
Linseed oil, raw	Hard brown or greenish brown clot.	Mottled, dark brown.
Linseed oil, boiled	Hard brown clot.	Mottled, dark brown.
Castor oil	Yellow to pale brown.	Nearly colorless, or pale brown.

COLOR REACTIONS OF ANIMAL OILS.

Lard oil............	Greenish yellow, or brownish with brown streaks.	Mottled or dirty brown.
Tallow oil..........	Yellow spot, with pink streaks.	Orange red.
Whale oil	Red, turning violet.	Brownish red, turning brown or black.
Seal oil............	Orange spot, with purple streaks.	Bright red, changing to mottled brown.
Cod-liver oil........	Dark red spot, with purple streaks.	Purple, changing to dark brown.
Sperm oil	Pure brown spot, with faint yellow ring.	Purple, changing to reddish or dark brown.

COLOR REACTIONS OF HYDROCARBON OILS.

Petroleum lubricating oil...........	Brown.	Dark brown, with blue fluorescence.
Shale lubricating oil	Dark reddish brown.	Reddish brown, with blue fluorescence.
Rosin oil, brown....	Bright mahogany brown.	Dark brown, with purple fluorescence.
Rosin oil, pale......	Mahogany brown.	Red brown, with purple fluorescence.

209. Sulphuric-Acid Color Test.—Of color tests, that with concentrate sulphuric acid is one of the most valuable and readily applied. Table 7 shows the effect produced on placing a drop or two of sulphuric acid in the center of about 20 drops of the oil, and observing the color both before and after stirring. The reactions described include those produced by the majority of hydrocarbon oils. As already stated, the colors produced by different samples of the same kind of oil are liable to considerable variation.

The reactions of oils with concentrate sulphuric acid are sometimes complicated or rendered indistinct by the charring action exerted by the reagent. This may be avoided by dissolving 1 drop of the oil in 20 drops of carbon disulphide, and agitating the solution with a drop of sulphuric acid. Whale oil, thus treated, gives a fine violet coloration, quickly changing to brown; whereas, with sulphuric acid alone, a mere red or reddish-brown color changing to brown or black is obtained.

210. Nitric-Acid Color Test.—The color reactions of oils with nitric acid are sometimes characteristic, especially in the case of seed oils. The test is recommended to be applied in various ways, but perhaps those methods that combine observations of the color and the character of the elaidin are to be preferred. Thus, O. Bach agitates 5 cubic centimeters of the sample with an equal volume of nitric acid, Sp. Gr. 1.30. After noting any coloration, the mixture is immersed in boiling water for 5 minutes and the effect again observed. A more or less violent reaction often occurs on heating, even resulting, as in the case of cotton or sesame oils, in the mixture being projected from the tube. The results of this method, obtained by Bach, are given in Table 8.

TABLE 8.

Oil.	After Agitation With Nitric Acid.	After Heating For 5 Minutes.	After Standing 12 to 18 Hours.
Olive oil	Pale green	Orange yellow	Solid
Arachis oil ...	Pale rose	Brownish yellow	Solid
Rape-seed oil.	Pale rose	Orange yellow	Solid
Sesame oil....	White	Brownish yellow	Liquid
Sunflower oil.	Dirty white	Reddish yellow	Buttery
Cottonseed oil	Yellowish brown	Reddish brown	Buttery
Castor oil	Pale rose	Golden yellow	Buttery

A similar test has been described by Massie, who agitates 10 grams of the oil with 5 cubic centimeters of nitric acid, Sp. Gr. 1.40, and 1 gram of mercury, and observes the color

of the product after 1 hour, and also the time required for solidification. The results thus obtained are given in Table 9.

TABLE 9.

Oil.	Coloration.	Minutes for Solidification.
Olive oil.............	Pale yellowish green	60
Hazelnut oil..........	White	60
Almond oil...........	White	90
Arachis oil...........	Pale reddish	105
Apricot oil...........	Rose	105
Rape-seed oil.........	Orange	200
Cottonseed oil........	Orange red	105
Sesame oil	Yellowish orange	150
Beechnut oil	Reddish orange	360
Poppy-seed oil........	Red	Fluid

211. Nitric and Sulphuric Acid Color Test.—A mixture of strong sulphuric and nitric acids, used in the proportion of 1 drop to 10 drops of the oil, has been proposed by H. Meyer as a color test for certain fish oils. The following reactions were obtained with this test:

TABLE 10.

Oil.	Sp. Gr. of Sample.	Before Stirring.	After Stirring.
Cod-liver oil..	.9290	Violet, quickly becoming rose red.	Rose red, changing to light brown.
Hake-liver oil.	.9270	Dark violet, changing to dark brown.	Brownish violet, changing to light brown.
Skate liver oil.	.9320	Light violet, changing to brown.	Brownish violet, changing to brown.
Shark-liver oil	.9285	Light brown, with spots of red.	Light brown, becoming darker.
Herring oil...	.9326	Brown.	Dark brown.
Sprat oil......	.9284	Light brown.	Unchanged.
Seal oil.......	.9245	Light brown.	Lemon yellow, changing to emerald green and bluish green.
Whale oil.....	.9301	Light brown.	Darker.

CLASSIFICATION OF FATS.

212. Fats may be divided into two classes, viz., **liquid fats** and **solid fats.** The former are again subdivided into four subsidiary classes, viz., *drying oils*, *non-drying oils*, *fish oils*, and *fluid waxes*.

LIQUID FATS.

213. Drying Oils.—Many oils thicken on exposure to air, and, under favorable circumstances, gradually dry up into yellowish, transparent varnishes or resins, thereby absorbing considerable oxygen; they mainly consist of glycerides of linoleic acid, but they do not yield elaidin. Oils that possess this property are termed **drying oils.**

214. Non-Drying Oils.—These oils contain much olein, and dry with the utmost difficulty in the air or at higher temperatures. They absorb only small quantities of oxygen, but form elaidin.

215. Fish Oils.—**Fish oils** are obtained from the fat of fish; they absorb considerable quantities of oxygen, but do not dry up to a varnish on exposure to air, and yield little or no elaidin. They give intense colorations with caustic soda, sulphuric acid, nitric acid, and phosphoric acid, of which that obtained with the latter acid serves conditionally to distinguish them from other oils. It is obtained by warming 5 volumes of oil with 1 volume of glacial phosphoric acid. By this treatment, all fish oils, whether mixed or not, give an intense red, brown-red, or brown-black shade.

216. Fluid Waxes.—**Fluid waxes** obtained from the oil of marine animals consist mainly of esters of monatomic alcohols, and contain only a small amount of glycerides. They are, like true waxes, only partially saponifiable, and possess, in consequence, a very low saponification number. The unsaponified portion is solid and consists of monatomic alcohols. They contain only 60 to 65 per cent. fatty acids, as against 95 per cent. in other oils. They absorb very little

oxygen when exposed to air, do not dry to a varnish, and give no elaidin.

217. Recognition of Drying and Non-Drying Oils. For testing drying properties of oil, a definite number of drops of the sample may be placed in a watch glass and exposed to a temperature of about 100° for from 12 to 24 hours, side by side with samples of oil of known purity. Olive oil will scarcely be affected by such treatment, and rape oil will only thicken somewhat. Cottonseed oil will be considerably affected, while good linseed oil will form a hard skin or varnish, that can only be ruptured with difficulty by pressure with the finger. In some respects, a preferable plan is to flood a thin piece of glass with the oil. The glass with the adhering film of oil is then kept at 100° and the progress of drying watched by touching, at intervals, successive parts of the plate with the finger.

These methods require, however, a great deal of time, and the determinations hardly furnish a sure means of recognition, so that the elaidin reaction is preferable in any case.

218. Elaidin Reaction.—When oleic acid is treated with a few bubbles of nitrogen trioxide, it is gradually changed into the isomeric body, elaidic acid, which is solid at ordinary temperatures. Olein undergoes a similar change with production of the solid isomeric elaidin, as also do such oils as consist of olein in a state of approximate purity. On the contrary, the drying oils, which consist chiefly of the glycerides of linoleic acids, are not visibly affected by treatment with nitrous acid. Oils that probably consist of mixtures of olein with more or less linolein give less solid products with nitrous acid than the approximately pure oleins.

The following method of obtaining the elaidin reaction, due to Poutet, has been studied by Archbutt, and is undoubtedly one of the best.

Mercury to the amount of 1 cubic centimeter should be dissolved in 12 cubic centimeters of cold nitric acid of 1.42

Sp. Gr.; 2 cubic centimeters of the freshly made, dark-green solution is then shaken into a wide-mouthed stoppered bottle with 50 cubic centimeters of the oil to be tested, and the shaking repeated every 10 minutes during 2 hours. When treated in this manner, oils consisting of approximately pure olein, or of mixtures of olein with the solid esters, such as palmitin and stearin, give a solid product of greater or less consistency. Olive oil is remarkable for the canary, or lemon-yellow, color and great firmness of the elaidin yielded by it. After 24 hours, the hardness of the product is such that it is impervious to a glass rod, and sometimes rings when struck with it, but this characteristic is also possessed by the elaidins yielded by arachis and lard oils. In making the elaidin test, it is important to note the time required to obtain a solid product that will not move on shaking the bottle, as well as the time required for its ultimate consistency. Also, the temperature should be kept as nearly constant as possible, or erratic results may be obtained, and comparison of different oils becomes impossible.

The behavior of the various more important liquid fats is as follows: A hard mass is yielded by olive, almond, lard, sperm, and sometimes neat's-foot and arachis oils. A product of the consistency of butter is given by neat's-foot, mustard, and sometimes by arachis, sperm, and rape oils. A pasty or buttery mass that separates from a fluid portion is yielded by rape, sesame, cottonseed, sunflower, niger-seed, cod-liver, seal, whale, or porpoise oil. Liquid products are yielded by linseed, hemp-seed, walnut, and other drying oils.

219. Maumené's Test.—This test depends on the phenomenon that sulphuric acid, mixed with drying oils, heats up considerably more than with the non-drying oils. The following method of performing Maumené's test is that recommended by Archbutt and has been successfully employed by the writer:

Into a beaker of 200 cubic centimeters capacity is weighed 50 grams of the oil under examination, and the beaker immersed in a capacious vessel of water, together with a

bottle of strong sulphuric acid, until they are both at the same temperature, which should not be far from 20°. The beaker containing the oil is then wiped, and placed in a cotton-wool nest previously made for it in a cardboard box or wide beaker. The immersed thermometer is then observed, and the temperature recorded; 10 cubic centimeters of the concentrate sulphuric acid should then be withdrawn from the bottle with a pipette, and allowed to run into the oil. During the addition of the acid, which should occupy about 1 minute, the mixture must be constantly stirred with the thermometer, and the agitation continued until no further rise of temperature ensues. This point is readily observed, as the indication remains constant for 1 or 2 minutes, and the temperature then begins to fall. Should the rise equal more than 70°, drying oils can be considered present with certainty. As an example, olive oil shows a rise of 41° to 43° in temperature, rape oil 51° to 60°, and linseed oil 104° to 111°.

220. Iodine Number.—The non-drying oils possess lower iodine numbers than the drying oils. The iodine number, in consequence, serves as a convenient and safe means of identification, providing that fish oils are absent. These are non-drying, and yet possess a high iodine number.

SOLID FATS.

221. The recognition of the solid fats is accomplished chiefly by the (*a*) determination of specific gravity; (*b*) determination of melting and solidification points; (*c*) behavior in the refractometer; (*d*) determination of saponification and iodine numbers; (*e*) determination of volatile fatty acids by the Reichert-Meissl number.

222. Specific Gravity.—The specific gravity may be conveniently determined by the method of Gintl, who uses a small cylindrical flat-bottomed flask, the opening of which may be closed with a ground-glass plate. When filling in

the molten fat, an excess is allowed to remain above the top. After cooling, the plate is slipped on and screwed down. The excess is wiped off with a cloth dipped in petroleum ether. The weight of an empty flask, a flask filled with water at 15.5°, and a flask filled with the cooled fat are determined in the usual manner, and the specific gravity of the fat is obtained by dividing its weight by that of the water. For example:

Weight of flask, dry..........	10.0197 grams.
Weight of flask, plus water....	37.3412 grams.
Weight of water..............	27.3215 grams.
Weight of flask, plus fat......	34.6111 grams.
Weight of fat................	24.5914 grams.

Specific gravity $= 24.5914 \div 27.3215 = .90008$.

According to the method of Hager for the determination of specific gravity, the molten fat is drawn up into a pipette, from which it is allowed to drop slowly from the height of 1 inch into a glass dish filled with 60 to 90 per cent. of alcohol. The solidified drops are placed in the liquids, which serve to determine specific gravity. For densities less than water, a mixture of water and alcohol is used; and, for greater densities, a mixture of glycerine and water or alcohol is used. Glycerine or glycerine and water are added until the drop just floats on the liquid, which is set in rotation. Finally, the liquid is poured through glass wool, and the specific gravity, which is equal to that of the fat, is then determined by means of a hydrometer or pycnometer.

The great objection to this otherwise very ingenious method is that fat and waxes that have undergone sudden cooling have, very often, abnormal specific gravities; hence, the results cannot be too strictly relied on.

223. Melting and Solidification Points.—Full directions for the determination of the melting and solidification points will be given in the discussion of tallow and waxes.

224. Behavior in the Refractometer.—Valuable indications as to the identity and purity of fats and oils.

especially butter fat, may be gained from the determination of the refractive index. This may be done by means of Abbé's refractometer, shown in Fig. 44, observing the total

FIG. 44.

reflection that a thin stratum of the fat or oil placed between prisms of a more highly refractive substance produces in transmitting light. The following description of the method of using the instrument is taken from the bulletin of the Association of Official Agricultural Chemists.

A piece of fine tissue paper, 3 centimeters in length by 1.5 centimeters in width, is placed on the lower of the two prisms of the apparatus (not shown in the figure). On this paper are placed 2 or 3 drops of the fat or oil, and the upper prism is carefully fixed in position, so as not to move the paper from its place. In charging the apparatus with the oil in this way, it is placed in a horizontal position. After the paper holding the fatty substance is secured by replacing the upper prism, the apparatus is placed in its normal position

and the index moved until the light directed through the apparatus by the mirror shows the field of vision divided into dark and light portions. The dispersion apparatus *a* is now turned until the rainbow colors on the part between the dark and light fields have disappeared. Before doing this, however, the telescope *b* (the eyepiece of the apparatus) is so adjusted as to bring the cross-lines of the field of vision distinctly into focus. The index *c* of the apparatus is now moved back and forth until the line of the two fields of vision falls exactly at the intersection of the cross-lines. The refractive index of the fat under examination is then read directly on the scale *d* by means of a small magnifying glass. To check the accuracy of the first reading, the dispersion apparatus is turned through an angle of 180° until the colors have again disappeared, and, after adjustment, the scale of the instrument again read. These two readings should nearly coincide, and their mean is the true reading of the fat under examination.

For butter fats, the apparatus should be kept in a warm place, the temperature of which does not fall below 30°. For reducing the results obtained to a standard temperature, say 25°, the factor .000176 should be employed. As the temperature rises the refractive index falls. For example:

Refractive index of a butter fat determined at 32.4° = 1.4540, reduced to 25° as follows: $32.4 - 25 = 7.4$; $.000176 \times 7.4 = .0013$; then, $1.4540 + .0013 = 1.4553$.

The instrument used should be set with distilled water at 18°, the theoretical refractive index of water at that temperature being 1.333. In the determination given in the example, the refractive index of pure water measured 1.3300; hence, the given number should be corrected by the addition of .0030, making the corrected index of the butter fat mentioned, at the temperature given, 1.4583.

225. The following numbers in Table 11 show the refractive indexes for some of the more common oils, that of water being taken as 1.333 at 18°.

TABLE 11.

Name.	Temperature.	Refractive Index.	Calculated for 25°.
Olive oil (France)	26.6°	1.4673	1.4677
Olive oil (California)	25.4°	1.4677	1.4678
Cottonseed oil	24.8°	1.4722	1.4721
Cottonseed oil	26.3°	1.4703	1.4709
Cottonseed oil	25.3°	1.4718	1.4719
Sesame oil	24.8°	1.4728	1.4728
Sesame oil	26.8°	1.4710	1.4716
Castor oil	25.4°	1.4771	1.4773
Lard oil	27.3°	1.4657	1.4668
Peanut oil	25.3°	1.4696	1.4696

226. Volatile Fatty Acids.—A useful method of examining fats and oils consists in determining the amount of alkali required to neutralize the volatile fatty acids. These are determined by the Reichert-Meissl number, which represents the number of cubic centimeters of one-tenth normal alkali that is necessary to neutralize the volatile fatty acids in 5 grams of fat.

About 5 grams of fat are placed in a 200 to 300 cubic-centimeter flask on a water bath to which about 2 grams of potassium hydrate in sticks, chemically pure by alcohol, and 50 cubic centimeters of 70 per cent. of alcohol are added, and the whole saponified, shaking the flask at frequent intervals. After complete saponification, the heat is increased and the alcohol volatilized until a thick soap only remains in the flask. This is dissolved by heating gently with 100 cubic centimeters of water; 40 cubic centimeters of dilute sulphuric acid (1 : 10) and a few pieces of pumice stone are added and the flask connected, by means of a bulb tube, with a Liebig condenser. It is first heated with a small flame until the fats have melted to a clear layer, after which it is distilled and exactly 110 cubic centimeters of the distillate

are collected in a flask graduated thus. The time of distillation should be so regulated that it does not occupy less than 30 minutes. After thoroughly shaking up the contents of the flask, 100 cubic centimeters are filtered off into a measuring flask or cylinder, transferred to a beaker of appropriate size, and titrated with $\frac{n}{10}$ alkali, using phenol-phthalein as an indicator. The quantity of alkali used is increased one-tenth and calculated on exactly 5 grams of fat.

The Reichert-Meissl method is very frequently used to identify butter and cocoanut oils. Butter has a number ranging from 26 to 29; cocoanut oil, 7.

227. Detection of Hydrocarbon Oils.—The extensive and cheap production of various hydrocarbon oils suitable for lubricating purposes has resulted in their being largely employed for the adulteration of animal and vegetable oils. The hydrocarbons most commonly employed are:

1. Those produced from petroleum and by distillation of bituminous shale.
2. Those produced by the distillation of common rosin.
3. Neutral coal oil, being the portion of the products of the distillation of coal tar, boiling above 170°.
4. Solid paraffin, employed for the adulteration of beeswax and spermaceti, and used in admixture with stearic acid for making candles.

The presence of hydrocarbons in fats and fatty oils is detected (1) by the altered density of the sample, which is decreased by members of the first class and increased by rosin and coal-tar products; (2) by the lowering of the flashing and boiling point; (3) by the fluorescence of members of the first two classes; (4) and by the incomplete saponification by alkalies. The taste and odor, on heating, are also valuable indications.

Specific gravity is a character of some little value for detecting and approximately estimating hydrocarbon, but in practice the indications obtained are apt to be rendered

valueless by the employment of a mixture that has the same density as the oil to be adulterated.

The tendency of a hydrocarbon is to reduce the flashing and boiling points of the fixed oil, and, in some cases, a distinct separation may be effected by fractional distillation.

Fluorescence is a character of considerable value for detecting the presence of hydrocarbons. If undoubtedly fluorescent, the sample certainly contains some hydrocarbon, but the converse is not strictly true, as the fluorescence of some varieties can be destroyed by treatment, and some hydrocarbons possess no fluorescence whatever. Most of the hydrocarbons employed for lubricating purposes are strongly fluorescent, and the many others become so on treatment with an equal volume of strong sulphuric acid. A hydrocarbon possessing strong fluorescence may be evident in presence of a very large proportion of fixed oil; but, if any doubt exists, the hydrocarbon should be isolated in the manner described further on.

The fluorescence may usually be seen by holding a test tube filled with the oil in a vertical position in front of a window, and looking at the sides of the test tube from above. A better method, perhaps, is to lay a glass rod, previously dipped in the oil, down on a table in front of a window, so that the oily end of the rod shall project over the end of the edge of the table, and be seen against the dark background of the floor. Another plan is to make a thick streak of the oil on a piece of black marble, or glass plate, smoked at the back, and to place the streaked surface in a horizontal position in front of, and at right angles to, a well lighted window. Examined in this manner, very slight fluorescence is readily perceptible. If at all turbid, the oil should be filtered before applying the test, as the reflection of light from minute floating particles is apt to be mistaken for true fluorescence. In some cases, it is desirable to dilute the oil with ether, to which an exceedingly small amount of mineral oil is sufficient to impart a strong blue fluorescence. This is useful in the examination of very dark oils, as the color is reduced without the intensity of the fluorescence being

correspondingly decreased. If the oil is very dark, for example, a dark Gallipolio or brown rape-seed oil, it should be first refined by agitating it successively with small proportions of concentrated sulphuric acid, water, and solution of sodium carbonate, and subsequently filtering. In some cases, decolorization may be effected by warming the oil and agitating it with freshly burnt animal charcoal, the liquid being subsequently filtered.

It must be remembered that fluorescence is not perceptible by gas light, but may be brought out by burning a piece of magnesium ribbon in the proper position.

228. Quantitative Estimation of Hydrocarbon Oils. The quantitative analysis of mixtures of fat or fatty oils with hydrocarbons is best carried out by the following method, which combines rapidity, certainty, tolerable accuracy, and general applicability, and, at the same time, furnishes the hydrocarbons in a condition for further examination.

The hydrocarbons that are to be determined are all unaffected by alkalies, whereas animal and vegetable oils and waxes undergo saponification. If potash or soda is employed, the resultant soap is soluble in water. The hydrocarbons, though insoluble in water and unaffected by alkalies, dissolve with greater or less facility in concentrated solution of soap and are very imperfectly separated on dilution. They may, however, be dissolved out from the dry soap by ether, chloroform, carbon disulphide, benzene or petroleum spirit. In some cases, a good separation is obtainable, but, in others, a considerable quantity of soap passes into solution, especially if the solvent is employed at a temperature approaching the boiling point. This tendency of the soap to undergo solution may be avoided by treating the aqueous solution with the solvent instead of the dry soap.

The following are the details of the manipulation: Of the sample 5 grams are saponified by alcoholic alkali, the solution partly freed from alcohol, and transferred to a separator of about 200 cubic centimeters capacity, shown in Fig. 45, furnished with a stop-cock *a* below and a stopper *b* at the

top. The tube below the stop-cock should be ground or filed off obliquely, so as to prevent any liquid remaining in it. The liquid is diluted with water until it measures from 70 to 100 cubic centimeters. From 50 to 60 cubic centimeters of ether should be next added, the stopper inserted, the liquids thoroughly shaken and allowed to rest for a few minutes. As a rule, two well defined layers will form, the lower one brownish, consisting of the aqueous solution of soap, the upper of ether, containing any hydrocarbon in solution. Separation does not always occur readily, the liquid remaining apparently homogeneous, or assuming a gelatinous consistency.

FIG. 45.

In such cases, separation may be induced by thoroughly cooling the contents of the separator, by adding caustic-soda solution, by adding more ether and reagitating; or, if all these means fail, a few cubic centimeters of alcohol may be added, and a gentle rotary movement imparted to the liquid, avoiding complete admixture, when a rapid separation of the ethereal layer almost invariably occurs. The aqueous liquid is then run through the top into a beaker. About 10 cubic centimeters of water and a few drops of caustic-alkali solution are added to the ether that remains in the separator and the whole agitated. The washings are then run off in their turn, and, after repeating the treatment with water, which is removed by the tap as before, the ethereal solution is poured off through the mouth into a weighed flask. The aqueous liquid and washings are then returned to the separator and agitated with a fresh quantity of ether, which is washed and poured into the flask as before. The agitation of the soap solution is repeated once more, when the extraction of hydrocarbon oil will be complete.

The ethereal solution will usually be strongly fluorescent. The flask containing it is attached to a condensing arrange-

ment, and the greater part of the ether distilled off by immersing the flask in boiling water. When distillation has ceased, the condenser is detached and the flask placed on top of a drying oven, by which the rest of the ether is soon dissipated. Sometimes the hydrocarbon will contain globules of water, in which case the flask should be held horizontally, and rotated rapidly, so as to spread the oil over the sides in a very thin layer and facilitate the evaporation of the water. When no more water is visible and the smell of ether is only faintly perceptible, the flask is placed on its side in the drying oven for 10 to 15 minutes and weighed, when the increase of weight over the original tare gives the amount of hydrocarbon oil extracted. Sometimes it is very difficult to obtain a constant weight by the means just indicated. In such a case, instead of heating the flask on the drying oven, it should be kept on the bath of boiling water, and a moderate current of air, filtered by passing it through a tube containing cotton wool, should be blown through it by a second tube passing through the cork. The fittings are then detached, and the flask heated for a short time in the drying oven to constant weight. Prolonged heating should be avoided, as many hydrocarbons are sensibly volatile at 100°.

EXAMINATION OF COMMON FATS.

229. It is impossible, of course, in a work of this kind to lay out hard-and-fast schemes of analysis that will meet all requirements and fit for all cases, and, in the following articles, only indications and hints are given to assist the student. He will have to rely on his own judgment, assisted by what he has learned so far, as to how he must proceed in each particular case, and he will have to refer to works on analysis that treat especially on the analysis of oil, adulteration of commercial and food products, etc.

OLIVE OIL.

230. Olive oil is the extraction product of the fruit of the olive. It varies somewhat in its physical properties according to quality. The finest kinds have a pale-yellow

color with a tinge of green, are almost entirely odorless, and have a mild and agreeable taste; while inferior kinds have a greenish-yellow to brownish-red color, an unpleasant odor, and a decided acrid after-taste.

Olive oil is a type of the non-drying vegetable oils; it does not thicken to any extent when exposed to air, but gradually becomes rancid, a change that seems to be dependent, to a great extent, on the presence of certain albuminous and mucilaginous matters.

Owing to the steady demand, it is very often adulterated, and cottonseed oil is perhaps the most frequent adulterant, but arachis, sesame, poppy-seed, and rape-seed oils are also occasionally employed. Fish and lard oils, however, are seldom used.

231. In the examination of olive oil, the most valuable indications are its specific gravity, the saponification equivalent, the iodine number, the rise of temperature on treatment with sulphuric acid, and the elaidin test.

The specific gravity of olive oil varies appreciably with the quality, the most acid specimen possessing the lowest density. The range of specific gravity allowed by the American Pharmacopœia is between .915 and .918 at a temperature of 15.5°. In about eighty samples of genuine, unadulterated olive oil, examined by Archbutt, the specific gravity at 15.5°, compared with water at exactly the same temperature, never exceeded .917 and was rarely as high, while the lowest specific gravity .9136 was noticed in a sample containing 24.5 per cent. of free oleic acid. Hence, in judging the character of an olive oil from its specific gravity, the quantity of free acid should always be taken into consideration. Taking the average specific gravity of genuine neutral olive oil as .917, it appears that each 5 per cent. of free acid diminishes the specific gravity of the sample by, approximately, .0007. Adulteration of olive oil with rape oil will tend slightly to reduce the specific gravity of the sample, while the addition of such oils as cottonseed, sesame,

poppy-seed, etc. will increase it. A judicious admixture, however, of rape-seed and cottonseed oils will not affect the density of the sample, but the presence of any considerable proportion of rape-seed oil will sensibly raise the saponification equivalent of it.

Samples of genuine olive oil show an iodine absorption number ranging from 81 to 85, although California olive oil occasionally gives a somewhat higher number. If the iodine number and saponification equivalent correspond to the mean value given in Table 6, the oil, as a rule, may be accepted as pure. Should the saponification value correspond, but the iodine number lie above 85, adulteration with sesame, peanut, or cottonseed oil has been attempted, and should the saponification equivalent be lower than the mean in the table, and the iodine number higher, the adulterant is presumably rape-seed oil.

The elaidin test is also of great value. Pure olive oil yields, in less than 2 hours, at a temperature from 15° to 20°, a semisolid mass that cannot be displaced by shaking the bottle, and, within 24 hours, a solid and sonorous, pale-yellow or nearly white mass is produced.

With adulterated samples, the elaidin obtained is orange or dark red, and liquid or semisolid, or, not infrequently, a liquid layer is formed on the surface of the solid elaidin. The elaidin test is applicable to the detection of sesame, rape-seed, cottonseed, poppy-seed, and linseed oils when in admixture with olive oil.

The admixture of hydrocarbon oils to olive oil destined for lubricating purposes is detected according to Arts. **227** and **228.** When used for this purpose, the acid number should be determined, and should not exceed 16.

The rise of temperature on treating a sample of olive oil with sulphuric acid is a valuable indication of its purity. Almost all oils, except lard and tallow oils, and cocoanut olein, produce more heat than olive oil, so that a rise of temperature of more than 44° may be considered as indicating probable adulteration.

RAPE-SEED OIL.

232. Rape-seed, or **rape, oil** is obtained from the seeds of several species of *Brassica*, of the order *Cruciferæ*. The seeds are commonly subjected to steam heat before pressure, to coagulate the albuminous matter and facilitate the extraction of the oil.

When freshly expressed, rape oil is a yellowish-brown or brownish-green viscid liquid, of a peculiar odor and pungent taste, owing to the foreign matter present. These impurities separate to some extent by keeping the oil, but are not entirely removed by passive treatment. They lessen the combustibility and cause much smoke during combustion. Brown rape oil or sweet rape oil is the commercial name for the oil expressed from the seeds. It is usually refined by treatment with sulphuric acid, and sometimes supplemented by agitation with alkali, and, of late years, a current of steam has been successfully applied. The refined oil is very light yellow and should be almost odorless. It takes an intermediate position between drying and non-drying oil. It does not thicken readily when heated and exposed to air, and yet gives but an imperfect solid elaidin with nitrous acid. In non-drying character, it is decidedly inferior to olive oil, but superior in odor and appearance to the lower qualities of the latter. Notwithstanding a slight tendency to gum, it is extensively used for engine and machinery lubrication, as well as for lighting purposes.

233. Assay of Commercial Rape Oil.—Rape oil is subject to numerous adulterations, the more important of which can be detected with tolerable certainty. The specific gravity of genuine oil averages .915 at 15.5°, and its specific gravity is a valuable indication of its purity, as all the ordinary adulterants are heavier than the genuine oil, with the exception of mineral oils, which can be readily detected and determined according to Arts. **227** and **228.** Foreign seed oils of more or less drying character, as sesame, sunflower, cress-seed, hemp-seed, cottonseed, linseed, and possibly cocoanut olein, all range between .920 and .937 in density.

Hence, if the sample has a specific gravity of .918, it may possibly contain even 50 per cent. of these oils, while the smell and color would be but little affected. Seed and nut oils deteriorate rape oil by increasing its gumming properties, with the exception of arachis oil and cocoanut olein, and the addition of either of these is improbable.

The normal values for the iodine number and saponification equivalent, as a rule, together with the specific gravity, suffice for identification. The increase of temperature on treating genuine rape oil with sulphuric acid averages 59°, the extreme variations being from 55° to 66.7°. Any greater rise than that which corresponds to the rise normally yielded by rape oil under the conditions of the experiment may be due to an admixture of cottonseed, hemp-seed, or linseed oil.

With the elaidin test, rape oil behaves in a peculiar and somewhat characteristic manner. Solidification occurs very slowly; but, after 50 or 60 hours, the oil is frequently converted into a pasty mass, which is sometimes yellow, and, in other cases, orange red or mottled. A separation into a solid and liquid portion frequently occurs. The results are much influenced by the temperature. At 10° many samples become apparently solid, but, on being touched with a glass rod, are seen to be a peculiar mixture of liquid and solid. On immersing the bottle containing the product formed at 10° for a short time in water at 15°, the elaidin forms a thick liquid.

The color test with sulphuric and nitric acids are of value for the detection of certain admixtures, such as linseed and fish oils. Richter states that on shaking 5 cubic centimeters of a sample with 1 cubic centimeter of solution of soda of Sp. Gr. 1.34, pure rape oil forms a dirty milky fluid, hemp oil a brownish-yellow thick soap, and train oil a dark-red solution.

CASTOR OIL.

234. Castor oil is expressed from the seeds of *Ricinus communis*. It is a transparent, colorless, or pale greenish-yellow liquid with a faint odor and disagreeable taste. At a

low temperature, it thickens, and, at $-18°$, it solidifies to a yellow mass. It is distinguished in its physical character from most other oils by its high specific gravity and viscosity, ready solubility in alcohol, and insolubility in petroleum spirit. These characteristics are of value for the assay of commercial samples.

235. The peculiar physical characteristics of pure castor oil distinguish it sharply from most other oils, but it is liable to adulterations, which, when not in excessive proportion, are very difficult to detect. The most probable adulterants are poppy oil, lard oil, cocoanut oil, seal oil, rosin oil, and the oxidized, or "blown," oil now manufactured from rape-seed, linseed, and cottonseed oils.

The specific gravity of pure castor oil ranges from .960 to .964, and any sample showing less than .958 is open to suspicion. The only other commercial fixed oil having as high a specific gravity is "blown" oil. Rosin oil has often as high a specific gravity as .998, but it can be readily detected and determined as described in Arts. **226** and **227.** Iodine number, saponification equivalent, and acetyl number, in connection with the specific gravity, serve to determine its purity. The acetyl number should not exceed 15.2.

It is generally claimed that pure castor oil must completely dissolve in 2 parts by volume of 95-per-cent. alcohol. This description is faulty; at a temperature of 30°, it is strictly correct, provided the volume and strength of alcohol and temperature are strictly adhered to, but the use of a slightly weaker alcohol, the addition of the smallest quantity of water, or a slight reduction of temperature causes the castor oil to be thrown out of solution. It is perhaps preferable to use 4 volumes of alcohol at 15° than half that volume at a higher temperature. If any considerable proportion of adulterant is present, the liquid separates, on standing, into three layers, of which the lowest is usually the adulterant and its volume will afford an approximate indication of the proportion of the admixture.

Castor oil is also readily soluble in glacial acetic acid. It is

easily miscible with an equal measure of that solvent at the ordinary temperature; whereas, most other fixed oils, except croton oil, are only dissolved on heating, and yield solutions that become turbid before they have again cooled to the ordinary temperature.

The behavior of castor oil with petroleum spirit is very characteristic. As far as known, all other fixed oils dissolve with facility in this solvent and appear to be miscible in all proportions therewith and with mineral lubricating oil. Castor oil, however, is not soluble in petroleum spirit, though it is itself capable of dissolving its own volume of that liquid. With the heavier petroleum and shale products, castor oil behaves in a similar manner, at least in a qualitative sense. In making a mixed oil for lubricating purposes, the castor oil must first be dissolved in an equal measure of tallow or lard oil, and the heavy mineral subsequently added. If the proportion of this does not exceed that of the castor oil employed, no separation will occur on standing.

SESAME OIL.

236. **Sesame oil** has a yellow color, is thinner than most oils, nearly odorless, and has a bland and agreeable taste. That expressed from the seeds congeals at about $-5°$, but that extracted by solvents congeals at about $+5°$. Its specific gravity ranges from .921 to .924. It is frequently adulterated with cottonseed oil. Neither the iodine number, saponification equivalent, nor the specific gravity affords sufficient means for identification, but the *Livache test* is particularly suited to this purpose. It depends on the fact that the increase in weight due to absorption of oxygen is perceptibly less in the presence of cottonseed oil than in the genuine article.

237. **Livache's Test.**—The test of Livache is conducted by precipitating the solution of a lead salt with zinc. The precipitate is quickly washed with water, alcohol, and ether, and dried in a vacuum over sulphuric acid. Two quantities of the lead powder, each 1 gram, are spread out in a thin

layer on two large watch glasses. The weight of the glass and powder of each are taken, and, by means of a finely drawn out pipette, 20 drops of the oil in question are placed on one watch glass in such a manner that the drops do not flow together. On the other glass, a similar quantity of sesame oil, known to be strictly pure, is placed and both are again weighed. They are then allowed to stand at the ordinary temperature, in a place exposed to light but protected from dust, for 7 days. When the time has elapsed, the increase in weight of each is determined and reckoned in percentage of the substance. If the substance under examination was pure, the percentage will be the same as that of the standard, but, in the case of adulteration with cottonseed oil, the percentage will be perceptibly smaller.

238. Detection of Sesame Oil in Other Fatty Substances.—Olive oil and sometimes butter are mixed with the cheaper body, sesame oil. The latter is detected with certainty from the red coloration it gives when mixed with furfurol and hydrochloric acid. Instead of furfurol, some body yielding it when subjected to the action of hydrochloric acid, viz., sugar, may be used. It has been found, however, that an alcoholic solution of 2 grams of furfuraldehyde in 100 cubic centimeters of alcohol is the best reagent; $\frac{1}{10}$ cubic centimeter of this reagent is used for each test.

The test is made as follows: The quantity of the furfuraldehyde solution mentioned above is mixed with 10 cubic centimeters of hydrochloric acid, and there is added, without mixing, an equal volume of the suspected substance. On standing, a red coloration is produced at the zone of separation of the two liquids. If the oil is sesame, the coloration is produced instantly. As little as 1 per cent. of sesame oil in a mixed oil will show the color in 2 minutes.

ARACHIS OIL.

239. Arachis, earthnut, or peanut, oil is obtained from the nuts of *Arachis hypogæa*, an herb indigenous to America, but now cultivated in various countries, the oil being chiefly

expressed in France. The seeds contain about 45 per cent. of oil, which in India is known as *katchung oil*, and is largely used there as a substitute for olive oil. Arachis oil is usually pale greenish yellow, and of a peculiar nutty flavor and smell, but may be prepared nearly colorless and almost tasteless. It becomes turbid at about 3° and solidifies at about −5°. Its specific gravity ranges between .916 and .920.

240. Arachis oil is characterized by the iodine number and saponification equivalent given in the tables as well as the rise of temperature, which equals 45.5° to 51.4° with Maumené's test. Additions of peanut oil to other oils can be detected according to De Negri and Fabris by the fact that the soap solutions obtained in the determination of the saponification number solidify comparatively easy. An olive oil diluted with 10 per cent. of peanut oil after determination of the saponification number gives a turbid liquid that subsequently deposits a precipitate of the potassium salt of arachic acid.

COTTONSEED OIL.

241. Cottonseed oil is now produced in enormous quantities in this country and Europe and is used in large quantities in the manufacture of margarine, as adulterant of olive oil, in ointments, and for culinary purposes.

Crude cottonseed oil has a specific gravity of .916 to .930 and contains in solution a characteristic coloring matter, which gives it the ruby-red color. The crude oil gives a bright-red coloration with sulphuric acid and the soap from it rapidly oxidizes on exposure to air with the production of a fine purple or violet-blue color. This reaction is characteristic. It is this coloring matter that causes the oil to produce stains, and it may be removed by shaking the crude oil, at ordinary temperature, with about 10 per cent. of its volume of a solution of caustic soda of Sp. Gr. 1.06, when the alkali combines with the coloring matter and saponifies a portion of the oil. The mixture becomes filled with black flocks, which settle on standing and leave the oil but slightly

colored. The loss from refining is usually from 4 to 7 per cent., although, occasionally, losses of 12 to 15 per cent. occur. It is, therefore, desirable, before purchasing crude cottonseed oil for refining, to make a laboratory test in order to establish approximately the loss that will occur with that particular lot of oil.

Refined cottonseed oil has a specific gravity ranging from .922 to .926, and it solidifies at from 1° to 10°. Its color varies from very pale yellow to golden yellow. By subjecting the oil to cold and pressure, a certain proportion of stearin is separated, and the melting point of the residual oil consequently lowered. This refined oil is usually free from acid, and, when properly prepared, of pleasant taste and well adapted for culinary purposes.

Cottonseed oil is not in itself very liable to adulteration, but is very frequently employed to adulterate other higher prized oils. It may be detected by the specific gravity together with color tests given below and those given in Arts. **208** to **211**, and in the tables in connection with these articles.

242. Bechi's Test for Detection of Cottonseed Oil. Crude, fresh cottonseed oil, when not too highly colored, as well as the refined oil, may be distinguished from other oils by the peculiar property of reducing silver salts in certain conditions. The test is conducted as follows: Silver nitrate to the amount of 1 gram is dissolved in 200 cubic centimeters of 98-per-cent. alcohol and 40 cubic centimeters of ether, and 1 drop of nitric acid is added to the mixture; 10 cubic centimeters of the oil under examination are shaken in a test tube with 1 cubic centimeter of this reagent, and then with 10 cubic centimeters of a mixture containing 100 cubic centimeters of amyl alcohol and 10 cubic centimeters of rape-seed oil. The mixture is divided into two portions, one of which is put aside for future comparison and the other plunged into boiling water for 15 minutes. A deep brown or black color, due to the reduction of silver, reveals the presence of cottonseed oil. Unless cottonseed oil has

been boiled or refined in some unusual way, the test, as applied above, is rarely negative.

243. Nitric-Acid Test.—On shaking cottonseed oil with nitric acid of Sp. Gr. 1.37 to 1.38, a rich brown coloration is produced. The coloration is equally distinct in the case of oils that have been boiled, and, in this respect, the test is superior to Bechi's. Occasionally, however, samples of American cottonseed oil are found that react so faintly with nitric acid as to make it impossible to detect adulteration by them to the extent of 10 per cent. In doubtful cases, both tests should be applied, and if uncertain results are obtained, Halphen's test, given in Art. **244**, should be used.

244. Halphen's Test.—Carbon disulphide, containing about 1 per cent. of sulphur in solution, is mixed with an equal volume of amyl alcohol. Equal volumes of this reagent and the oil under examination, say 3 cubic centimeters of each, are mixed and heated in a bath of boiling brine for 15 minutes. If no red or orange tint is produced, 1 cubic centimeter of the reagent is added, and, if after 5 to 10 minutes more heating no coloration is produced, another 1 cubic centimeter of the reagent is added, and the boiling continued for 10 minutes. It is possible to detect very small quantities of cottonseed oil by this test.

TALLOW.

245. Tallow is commercially classed as *beef* and *mutton* tallow, but each of these comprises the fat of other animals besides the ox and the sheep. Pure tallow is white and almost tasteless, but much of that in commerce has a more or less yellow color and disagreeable rancid flavor. In chemical composition, tallow is very similar to lard, consisting essentially of a mixture of palmitin, stearin, and olein.

246. In addition to the constants, viz., specific gravity, iodine number, and saponification equivalent, the determina-

tion of the freezing point of the fatty acids, the so called *titer test*, is of especial importance. In order to obtain concordant results, the following method was proposed by Wolfbauer: 25 cubic centimeters of potassium-hydrate solution, Sp. Gr. 1.509 (125 grams of potassium hydrate in sticks in 100 cubic centimeters of water), are stirred with 120 grams molten sample in a beaker. The temperature should only vary slightly above the melting point of the tallow. It is placed in an oven at 100°, after being agitated, mixed, and covered with a watch glass where it is permitted to remain, with occasional stirring, until saponification is complete, and a drop warmed with 50-per-cent. alcohol completely dissolves, which is the case after about two hours. 150 cubic centimeters of boiling water are stirred into the soap, which is then poured into a dish, treated with 165 cubic centimeters of sulphuric acid, Sp. Gr. 1.143 (22 cubic centimeters of concentrate sulphuric acid and 150 cubic centimeters of water), and boiled until the fatty acids form a perfectly clear layer.

The acid liquor is withdrawn entirely with a siphon and the fatty acids are boiled with weak sulphuric acid (5 cubic centimeters of concentrate sulphuric acid in 100 cubic centimeters of water), which is again withdrawn, after which they are twice boiled out with 100 cubic centimeters of water. The fatty acids are eventually dried for 2 hours at 100°. The solidified acids are melted in a water bath and filled to within 1½ centimeters into a thin-walled test tube 15 centimeters in length and 3.5 centimeters in diameter. The test tube is then suspended in a specimen bottle by means of a cork. Thereupon a thermometer, graduated to one-fifth degrees as far as 60°, is inserted through the cork into the fatty acids in such manner that, while ¾ centimeter distant from the bottom, it is submerged to the 35th division.

The clear mass is stirred with the thermometer until no longer transparent, and until the thermometer reading on repeated stirring no longer changes. The thermometer is then fastened. The mercury begins to rise, due to liberation

of latent heat of fusion. The highest mark that it touches, and at which it becomes stationary, is read off and taken as the "freezing point." The difference between two determinations should not exceed .1°.

The manipulation requires considerable skill and practice. Frequently, the iodine number of the fatty acids of tallow is taken. The number obtained multiplied by 1.1102 gives the oleic acid in the fatty acids. When used for lubricating purposes, tallow should not contain more than .5 per cent. of matter insoluble in chloroform.

WAXES.

247. As has been previously mentioned, **waxes** are of animal and vegetable origin. They are partly saponifiable and separate insoluble higher fatty alcohols. Mineral waxes are unsaponifiable. The saponification number affords a sure basis of distinction.

VEGETABLE AND ANIMAL WAXES.

248. The following determinations are usually made in the examination of vegetable and animal waxes.

1. Acid number.
2. Saponification number.
3. Ester number, which is the difference between the acid and saponification numbers.
4. Specific gravity.
5. Melting and freezing points.

The determinations are generally conducted according to the methods previously described.

249. Specific Gravity.—The specific gravity of waxes is most conveniently determined by means of a Sprengel tube, which has been shown in Fig. 2, *Physics*. A somewhat modified form is shown in Fig. 46, and consists of a U tube of about 18 cubic centimeters capacity and 11 millimeters external diameter, which tapers at both ends to

narrow bent tubes *a* and *b*, of which one is longer and is provided with a mark *m*. The molten fat or wax is brought into the tube by suction, as shown in Fig. 3, *Physics*. It is then brought into a water bath of constant temperature, until the wax ceases to expand, and the excess in the shorter arm is removed with filter paper, until the longer arm is just filled to the mark. It is allowed to cool, the tube is carefully wiped clean, and weighed. The experiment is repeated with water. The specific gravity from these data is obtained according to Art. **36**, *Physics*.

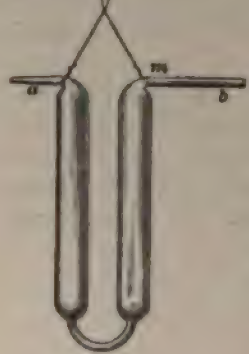

FIG. 48.

250. Melting Point.—Many methods have been devised for determining the melting point of fats, but none has been found that really is satisfactory in every respect. The following methods may be recommended for waxes:

The wax is carefully melted in a beaker, and a capillary tube is dipped into the liquid fat, and when filled, one end of the tube is sealed in the lamp and it is then put aside in a cool place for 24 hours. At the end of this time, the tube is tied to the bulb of a delicate thermometer, the length used or filled with fat being the same length as the thermometer bulb. The thermometer and attached fat are placed in water or other transparent media, and gently warmed until the capillary column of fat becomes transparent. At this moment, the thermometric reading is made, and entered as the melting point of the fat.

Another method consists in dipping a thermometer in the molten fat for a moment and thus obtaining the bulb covered with a thin film of the fat. The thermometer is then fixed in a test tube in such a way as not to touch the bottom, and the film of fat warmed by the air bath until it fuses and collects in a little drop at the end of the thermometer bulb, when the temperature is taken.

EXAMINATION OF BEESWAX FOR ADULTERANTS.

251. Total Acid Number.—In consequence of the difficulty experienced in the saponification of many waxes with alcoholic potash, especially when they contain paraffin and ceresin, too low results are frequently obtained. Benedict and Mangold therefore determine the "total acid number" instead of the "saponification number," that is, the number of milligrams of caustic potash required to neutralize 1 gram of the mixture of fatty acids and alcohol that is set free from the wax by saponification of the wax and subsequent decomposition of the soap obtained by boiling with dilute hydrochloric acid. The mixture is termed **decomposed wax.**

In order to prepare the latter, 20 grams of potassium hydrate are dissolved in 15 cubic centimeters of water in a hemispherical capsule of 350 to 500 cubic centimeters capacity. The solution is heated to boiling, when about 20 grams of the previously melted wax are stirred in. The solution is heated 10 minutes, with constant, brisk stirring, over a small flame; 200 cubic centimeters of water are added, the mass is heated and acidified with 40 cubic centimeters of hydrochloric acid, previously diluted with a little water. Thereupon it is boiled until the upper layer becomes perfectly clear. It is allowed to cool, and is boiled out 3 times with portions of water, to the first of which hydrochloric acid has been added. The cake is finally removed, wiped off with filter paper, is melted in a drying oven, and filtered. The filtered fat is poured, still liquid, on a watch glass, and is broken up after cooling. For the estimation of the total acid number, 6 to 8 grams of the decomposed wax so obtained are covered with alcohol, heated on a water bath, and titrated after addition of phenol phthalein. Even when a large amount of ceresin is present, the saponification is usually complete. The total acid number lies somewhat lower than the saponification number, on an average being about 92.8.

252. Ceresin and Paraffin.—The amount of paraffin or ceresin present may approximately be ascertained on the

basis of the total acid number S, by means of the following formula:

$$P = 100 - \frac{100\,S}{92.8}, \qquad (9).$$

where P = paraffin or ceresin, and 92.8 = average total acid number of pure beeswax.

The test of Messrs. Buisine is useful in the exact determination of the paraffin or ceresin. This depends on the fact that the fatty alcohols, on heating with soda lime, disengage hydrogen with the formation of the sodium salts of corresponding fatty acids according to the equation:

$$\underset{\text{cetyl alcohol}}{C_{15}H_{31}CH_2OH} + NaOH = \underset{\text{sodium palmitate}}{C_{15}H_{31}COONa} + 2H_2$$

A subsequent extraction with ether or petroleum spirit removes, besides paraffin and ceresin, only the hydrocarbons of the beeswax, which latter vary from 12 to 14.5 per cent.

To accomplish this, 2 to 10 grams of sample are melted in a small porcelain crucible, and to it is added an equal volume of powdered caustic potash. It is stirred, and on cooling a hard mass is obtained, which is pulverized and uniformly mixed with 3 parts soda lime (for 1 part of wax).

The mixture is then heated in a small flask at 250° for 2 hours. The residue, if necessary, together with the adhering broken glass of the flask, is powdered and extracted in a flask or extractor with ether or petroleum ether. The liquid is filtered, if necessary, the solvent is distilled off, and the last adhering traces of it are vaporized. The residue is then weighed. If p = percentage of hydrocarbons found, and C = ceresin or paraffin, then, if the hydrocarbons in genuine beeswax are taken as 13.5 per cent.,

$$C = \frac{100\,p - 1{,}350}{86.5}. \qquad (10.)$$

253. Stearic Acid.—Stearic acid heated with alcohol dissolves, together with ceresin, but, unlike the latter, it does not separate so readily on cooling.

Therefore, if 1 gram of wax be boiled for several minutes with 10 cubic centimeters of 80-per-cent. alcohol in a test

tube 18 to 20 millimeters wide, and allowed to cool to 18° to 20°, then upon adding water to the solution, filtered into a similar test tube, the liquid becomes slightly turbid if it contains pure wax, whereas, when stearic acid is present, a flocculent precipitate is formed. On the strength of the acid number, the stearic acid may be approximately determined by calculation. The acid numbers of pure beeswax and stearic acid are respectively 20 and 195.

If that of the sample = S, then the stearic acid equals

$$K = \frac{100(S-20)}{175}. \qquad \textbf{(11.)}$$

The absence of other acids is, of course, taken for granted.

MINERAL OILS.

254. Mineral oils are either distillation products of bituminous coal or bituminous shales, etc., or else their origin is crude petroleum, from which they are likewise obtained by distillation. Their use is mainly for lubricating and illuminating purposes. The higher distillation products of petroleum or shale, termed **heavy oils,** are used as lubricants, while the lower boiling fractions of shale oil are used for illuminating purposes, under the names of **solar oil, illuminating oil,** and those from crude petroleum, as **petroleum.**

The gas oils, likewise from shale oil, are used mainly in oil-gas factories, while the lowest distillation products (light shale oil, photogen on the one hand, gasolene, naphtha, benzine on the other) are used as solvents for fats, etc.

MINERAL LUBRICANTS.

255. The generally accepted conditions of a good lubricant are as follows:

1. Body enough to prevent the surfaces, to which it is applied, from coming into contact with each other.

2. Freedom from corrosive acids, either mineral, animal, or vegetable origin.

3. As fluid as possible consistent with "body."
4. A minimum coefficient of friction.
5. High "flash" and "burning" points.
6. Freedom from all materials liable to produce oxidation or gumming.

In order to identify the oil, whether a simple mineral, animal, or vegetable oil, or a mixture, the viscosity, specific gravity, flash point, burning point, acidity, rosin oils, coal-tar oils, are the tests usually undertaken.

256. Identification of Oil.—Of the oil, 10 grams are weighed out into a dry, weighed beaker of 250 cubic centimeters capacity, and to it are added 75 cubic centimeters of an alcoholic solution of potash (60 grams $NaOH$ to 1,000 cubic centimeters of 95-per-cent. alcohol), and the contents evaporated until all the alcohol is driven off. In this process, if any animal or vegetable oil is present, it is formed into a soap by the potash, while the mineral oil is unacted upon. Water, to the amount of 75 cubic centimeters, is then added, and the whole thoroughly stirred to insure complete solution of the soap, and it is then transferred to a separatory funnel, shown in Fig. 47, 75 cubic centimeters of sulphuric ether added, corked, the liquid violently agitated and allowed to stand for 12 hours. Two distinct liquids are now seen, the lower, the solution of the soap, the upper, the ether solution (colored, if mineral oil is present, colorless if not). The aqueous solution is drawn off in a beaker, the ethereal solution remaining in the separatory funnel. The former is placed on a water bath, heated

FIG. 47.

for half an hour or until all traces of ether are gone. The solution is allowed to cool, diluted somewhat with water, and made acid with dilute sulphuric acid. Any animal or vegetable oil present will be indicated by a rise of the fatty acids to the surface of the liquid.

If it is desired to weigh the fatty acids, proceed as follows: Weigh carefully about 5 grams of pure, white beeswax, place it in the beaker upon the surface of the oil and water, and bring the contents nearly to boiling; the melted wax and fatty acids unite; allow to cool, remove the wax, wash with water, dry between folds of filter paper, and weigh. The increase in weight of the wax over its original weight gives the weight of the fatty acids of the animal or vegetable oil in the lubricating oil. The weight obtained must be multiplied by .97, since the fatty acids exist in the oil as anhydrides and not as hydrates, the latter being the form in which they are weighed.

257. Instead of weighing the animal or vegetable oil, some chemists prefer to make use of the ether solution, determining the hydrocarbon oil directly, in which case the mode of procedure is as follows: After drawing off the soap solution from the separatory funnel, the ether solution is run into a weighed flask of about 250 cubic centimeters capacity, and the ether distilled off. The residue in the flask now consists of the mineral oil and some water.

It is quite difficult to get rid of all this water. Direct heating is inadmissible, since the water spurts up through the oil out of the flask and is lost. This can be overcome, however, by placing a glass tube through the stopper, in shape of the letter **S**. Any oil ejected against the tube or cork cannot escape, but returns to base of flask, while the heat is gradually increased in the flask and the water vaporized and passed out through the tube; three to four weighings are generally required before a constant weight is obtained. The former process is preferable, since it is performed much more rapidly than the latter, and the animal and vegetable oils are positively shown and can generally be identified.

Many lubricating oils contain as high as 20 per cent. of hydrocarbon oil, volatile at or below 100°. It is, of course, in the ether solution, and when the water is expelled from the oil, after the ether has been driven off, that a large proportion of the volatile hydrocarbon is vaporized. If, now, the animal or vegetable oil is not also determined, a serious mistake would be made, viz., reporting 20 per cent. of animal oil when it is volatile mineral oil.

258. Viscosity.—A useful physical test for oils is based on their relative **body**, or **viscosity**, a property that may be regarded as the converse of fluidity.

The first instrument for the determination of the viscosity of oils was probably that of Schubler. It consisted of a glass cylinder, open at the top, and drawn to a $\frac{1}{32}$-inch tube at the bottom. Having filled the cylinder with the oil to be tested, the time required for 100 cubic centimeters of the oil to flow out through the aperture was noted, and this figure was compared with that obtained from water under similar conditions, the latter being taken as 1.

The Pennsylvania Railroad Company's viscosity tests are made as follows: A 100-cubic-centimeter pipette is graduated to hold just 100 cubic centimeters to the bottom of the bulb. The size of the aperture at the bottom is then made such that 100 cubic centimeters of water at 37.5° will run out of the pipette down to the bottom of the bulb in 34 seconds. The pipette being obtained, the oil sample is heated to the required temperature, care being taken to have it heated uniformly, when it is drawn up into the pipette to the proper mark. The time occupied by the oil in running out, down to the bottom of the bulb, gives the test figure. A stop watch is convenient, but not essential, in making the test.

These pipettes, known as **Dr. Dudley's viscosity pipettes**, are used in many railroad laboratories in this country, but they are rather difficult to clean, and are not as convenient as the **Engler viscosimeter**, which is shown in Fig. 48. The vessel containing the oil under examination consists of a smooth box *A* of brass, provided with a lid *A'*.

Connected with the bottom is a 20-millimeter tube *a*, which is almost exactly 3 millimeters in width. It is usually made of brass, and is open at the top. It may be opened and closed by the plug *b*. Filled to the mark, the apparatus should hold 240 cubic centimeters. The box *A* is surrounded

FIG. 48.

by a jacket *B* made of brass, and is open at the top. This serves to hold suitable fluid, by which the contents of *A* can be brought to the desired temperature. The thermometers *t* and *t'* record the temperature of the oil to be tested and the liquid in the jacket. The apparatus rests on a tripod. The measuring flask *C*, under the exit tube, is provided in its neck with the marks 200 and 240.

Regulation of the Apparatus.—Water, to the amount of 240 cubic centimeters, is placed in the box, which has previously been cleaned with ether, alcohol, and water, and

plugged. The temperature is brought to 20°. To do this, the water contained in the jacket *B* is maintained at this temperature until the inner thermometer registers 20°. In the meanwhile, the flask is allowed to drain. It is then placed under the vent and the plug is withdrawn. The time, that elapses while the flask is being filled to the 200-cubic-centimeter mark is recorded in seconds. The time required to issue should be between 50 and 55 seconds, when the apparatus is properly constructed. The mean is taken of three determinations, which should not differ more than 15 seconds. This time is taken as 1.

Oil Test.—In the next operation, all moisture is removed from the box by drying and rinsing with alcohol, and then with ether. The apparatus is filled to the mark with the oil in question. It is then brought to the desired temperature by heating the jacket *B*, which may contain either water or oil. The temperature of the oil under examination must remain constant for at least 3 minutes before the operation is begun. Determination of the time of issue is then conducted as before.

The lowest grade of an oil that is to be used as a lubricant is, according to Engler, a degree of viscosity of 2.6 at 20°, when water = 1. With viscosity determination of lubricants, the rule holds good that the temperature used should lie near that which the oil will assume while in use (machine oil 50°, cylinder oil 150°, etc.).

Fatty oils, as well as lubricants, are subjected to viscosimetric tests. In many cases, such as rape-seed oil, for instance, the viscosity is so large and so constant that it may serve as a test for purity.

259. Specific Gravity.—The specific gravity of lubricants may vary within wide limits. As a rule, the greater the specific gravity of an oil, the higher will be its flash point and viscosity; but there are many exceptions. Lubricating oils from Russian petroleum have a higher viscosity than the products of similar density from American petroleum and shale oil. In the case of oils completely fluid at

ordinary temperature, the specific gravity may be determined by any of the usual methods. The density of the thicker and semi solid oils is best ascertained by filling a specific-gravity bottle to the brim with the warm oil. When it has cooled to a temperature of 15.5°, the stopper is inserted, and worked to and fro until it is forced home, the excess of oil gradually escaping through the perforation in the stopper, when the bottle may be wiped clean and weighed.

260. Flash and Burning Points.—The flash point is the degree of temperature at which ignitible volatile vapors are given off by an oil, producing a flash when brought into contact with a small flame. The fire test or determination of burning point is simply a continuation of the flash test until the oil permanently ignites. The mode of procedure is as follows: A porcelain crucible, 6 centimeters upper diameter and 6 centimeters high, is filled with the oil within 1 centimeter of the rim. The mercury bulb of a thermometer is then immersed, with the end 1 centimeter above the bottom, which is best accomplished by first resting the thermometer on the bottom of the crucible and subsequently raising it 1 centimeter. The crucible is warmed in a sand bath, and when the temperature has overstepped 120°, a small flame is passed over the surface of the oil at the same height as the crucible rim at every increase of 5°. As soon as the first faint explosion of oil-vapor-saturated air ensues, the flash point has been reached. The flame is enlarged, and when the temperature has increased 10° to 15°, it is passed over the surface at every 2° increase, until quiet ignition takes place. The burning point is so obtained. Drafts are prevented by screens of pasteboard.

The Standard Oil Company and the New York Produce Exchange use Saybolt's oil tester, which is furnished with an electric battery, where the oil is ignited by electric sparks passing over the oil.

The burning point of spindle oils should not lie under 150°, and that of machine oils not below 170°.

261. Acidity.—Mineral oils should be entirely free from acids. The acid remaining after the refining process is detected by shaking about 100 cubic centimeters of oil with an approximately equal volume of tepid water to which several drops of methyl orange have been added. The aqueous layer, after settling, will appear red.

262. Resins.—Incompletely refined oils resinify readily. A test for resinous matter can be conducted by placing 20 cubic centimeters of the oil, together with 10 cubic centimeters of sulphuric acid and 20 cubic centimeters of petroleum benzine, in a cylinder divided into 50 cubic centimeters, agitating, and allowing to settle. The increase in volume of the sulphuric acid is read off. With good oils, the increase usually amounts to 1.2 to 2.4 cubic centimeters; that is, 6 to 12 per cent. of the oil volume. Under no condition must it exceed 2.4 cubic centimeters, or 12 per cent.

The freezing point of an oil, which in use is subjected to winter temperature, is usually ascertained. Furthermore, the lubricating value is frequently determined by means of special complicated physical apparatus.

PETROLEUM (ILLUMINATING OIL).

263. Kerosene is the refined product from petroleum that distils over (in the refining process) after the lighter oils, naphtha, etc., have been separated, and is the principal oil in use for illumination. In color, it varies from standard white to water-white (colorless), and its commercial value is dependent upon its flash and burning point. In the oil trade, the burning or fire tests are classified as 110° F., 120° F., 150° F., and 300° F. The 150° F. is known as **headlight oil**, and the 300° F., as **mineral sperm** and **mineral colza.**

The requirements for mineral oils to be used in railroad illumination are as follows:

150° F. FIRE-TEST OIL.

The oil must conform to the following requirements:

1. It must have a flash test above 125° F.
2. It must have a fire test not below 150° F.
3. It must have a cloud test not above 0° F.
4. It must be water-white in color.
5. Its gravity must be between 44° and 48° Baumé at 60° F.

300° F. FIRE-TEST OIL.

The oil must conform to the following requirements:

1. It must have a flash test above 250° F.
2. It must have a fire test not below 300° F.
3. It must have a cloud test not above 32° F.
4. It must be standard white in color.
5. Its gravity must be between 38° and 42° Baumé at 60° F.

264. Cloud Test.—The cloud test is made as follows: Of the oil, 2 ounces are placed in a 4-ounce sample bottle, with a thermometer suspended in the oil. The bottle is exposed to a freezing mixture of ice and salt, and the oil stirred with the thermometer while cooling. The temperature at which the cloud forms is taken as the cloud test.

265. The requirements for the flash and fire tests for illuminating oil used for domestic purposes are not so rigid as for railroad practice. In fact, large quantities of oil, flashing below 110° F. are used, the cheaper price being an incentive. So dangerous are these oils with low flash points, that many states have passed stringent laws against their use. An oil with a fire test of 110° F. very often has a flash test of 90° F., and many oils with a fire test of 120° F. flash at or below 100° F. It is the flash point of an oil that makes it dangerous, and while the refiners of oils mark their product by the fire test, the law passed by many states specify the flash test as the requisite.

There is no absolute ratio between the flash and fire test of an oil, since while many illuminating oils have a high fire

and flash test, others may have a high fire and a low flash test.

266. Wisconsin Oil Tester.—The instrument that gives the best satisfaction in testing illuminating oils for the flash and fire tests is called the **Wisconsin oil tester,** and is shown in Fig. 49. It is officially described as follows: On the left side of the figure is shown the instrument entire. It consists of a sheet-copper stand 8½ inches high, exclusive of the base, and 4½ inches in diameter. On one side is an aperture 3½ inches high, for introducing a small spirit lamp *A* or, better, a small Bunsen burner. The water bath *D* is also of copper, 4⅛ inches high and 4 inches inside diameter. The opening in the top is 2⅞ inches in diameter. It is also provided with a flange ½ inch wide, which supports the bath in the cylindrical stand. The capacity of the bath is about 20 fluid ounces, this quantity being indicated by a mark on the inside. *C* represents the copper oil

FIG. 49.

boiler. The lower section is 3⅜ inches high and 2¾ inches inside diameter. The upper part is 1 inch high and 3½ inches in diameter, and serves as a vapor chamber. The upper rim is provided with a small flange, which serves to hold the glass cover in its place. The oil holder contains about 10 fluid ounces, when filled to within ⅛ inch of the flange which joins the oil cup and the vapor chamber. In order to avoid

reflection from the otherwise bright surface, the oil cup is blackened on the inside.

The cover C is of glass, and is $3\frac{5}{8}$ inches in diameter; on one side is a circular opening closed by a cork, through which the thermometer B passes. In front of this is a second opening $\frac{1}{4}$ inch deep, and $\frac{3}{4}$ inch in width on the rim, through which the flashing jet is passed in testing. A small jet, $\frac{1}{4}$ inch in length, furnishes the best means for igniting the vapor. Where gas cannot be had, the flame from a small waxed twine answers well.

267. The test should be applied according to the following directions: Remove the oil cup and fill the water bath with cold water up to the mark on the inside. Replace the oil cup and pour enough oil to fill it within $\frac{1}{8}$ inch of the flange joining the cup and the vapor chamber above. Care must be taken that the oil does not flow over the flange. Remove all air bubbles with a piece of dry paper. Place the glass cover on the oil cup, and so adjust the thermometer that its bulb shall be just covered by the oil.

If an alcohol lamp is employed for heating the water bath, the wick should be carefully trimmed and adjusted to a small flame. The rate of heating should be about 2° per minute, and in no case should it exceed 3°.

As a flash torch, a small gas jet, $\frac{1}{4}$ inch in length, should be employed. When gas is not at hand, employ a piece of waxed linen twine. The flame in this case, however, should be small. When the temperature of the oil has reached 85° F., the testings should commence. To this end, insert the torch into the opening of the cover, passing it in at such an angle as to well clear the cover, and to a distance about half way between the oil and the cover. The motion should be steady and uniform, rapid, and without pause. This should be repeated at every 2° rise of the thermometer, until the temperature has reached 95°, when the lamp should be removed and the testings should be made for each degree of temperature until 100° F. is reached. After this, the lamp may be replaced, if necessary, and the testings continued for each 2°.

The appearance of a slight bluish flame shows that the flashing point has been reached.

In every case, note the temperature of the oil before introducing the torch. The flame of the torch must not come in contact with the oil. The water bath should be filled with fresh, cold water for each separate test, and the oil from a previous test carefully wiped from the oil cup.

268. The test for ascertaining the igniting point should be conducted as follows: Fill the cup with the oil to be tested to within $\frac{1}{8}$ inch of the flange joining the cup and the vapor chamber above. Care must be taken that the oil does not flow over the flange. Place the cup into the cylinder, and adjust the thermometer so that its bulb shall be just covered by the oil. Place the lamp or gas burner under the oil cup. The rate of heating should not exceed 10° a minute below 250° F., nor exceed 5° a minute above this point. The testing flame described in the direction of ascertaining the flashing point should be used. It should be applied to the surface of the oil at every 5° rise in the thermometer, until the oil ignites.

269. Viscosity.—According to Engler, the viscosity of illuminating oil bears a direct relation to the speed of absorption in the wick. To conveniently determine this speed in an oil, therefore, the viscosity is taken. The Engler apparatus (shown in Fig. 48), possessing, however, a 1.8-millimeter exit, instead of 3 millimeters, is used.

270. Distillation Test.—The distillation test is conducted in a distilling bulb, shown in Fig. 50, having the following dimensions: Diameter of bulb, 6.5 centimeters; diameter of neck, 1.6 centimeters; length of neck, 15 centimeters. The side tube should be 10 centimeters long, .6 centimeter wide, and attached at an angle of 75°. The distance from the place of attachment to the level of the 100 cubic centimeters of oil, with which the flask is filled, should be 9 centimeters. The side tube is attached to a condenser of 1 centimeter average width, and 45 centimeters in length;

100 cubic centimeters of petroleum are placed in the bulb with a pipette, and are heated to boiling. A wire gauze is set under at first, but is removed when the temperature has risen above 150°. Distillation is conducted so that 2 to 2½ cubic centimeters distil over every minute. The fractions between every 25° or 50° are weighed or measured. As soon as a temperature of 150° is reached, the temperature is allowed to fall at least 20° by removing the lamp. The contents are again brought to boiling, and are distilled until the above temperature is again reached. This is repeated until nothing more distils over at that point. Results agreeing within 1 per cent. are thus obtained. The main fraction, distilling over at from 150° to 300°, is termed *illuminating oil*, which, in especially well refined illuminating oils, can reach 80 and even 90 volume per cent. A good illuminating oil should contain (according to Beilstein) not more than about 5 per cent. fraction under 150°, and not more than about 15 per cent. fraction above 270°.

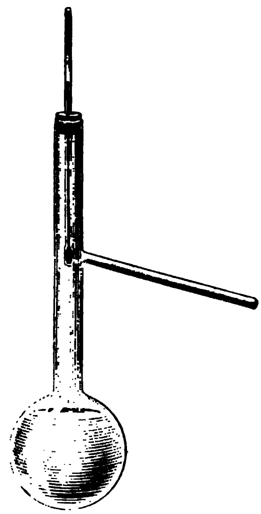

FIG. 50.

The test for acids can be conducted according to the method described under lubricating oils. The behavior toward concentrate sulphuric acid is at times used as a test for purity of petroleum. On mixing with an equal volume of concentrate sulphuric acid, and allowing to separate, the petroleum layer should be rather lighter, and the sulphuric acid at the most only yellow, but never brown. The rise of temperature on mixing should not exceed 5°. A rise of temperature of 20° to 50° ensues when distillates of bituminous shales, rosin, etc. are present.

A SERIES

OF

QUESTIONS AND EXAMPLES

RELATING TO THE SUBJECTS
TREATED OF IN THIS VOLUME.

It will be noticed that the various Question Papers that follow have been given the same section numbers as the Instruction Papers to which they refer. No attempt should be made to answer any of the questions or to solve any of the examples until the Instruction Paper, having the same section number as the Question Paper in which the questions or examples occur, has been carefully studied.

QUALITATIVE ANALYSIS.

(PART 1.)

(1) Define qualitative analysis.

(2) What metals impart the following colors to the borax bead: (*a*) green, (*b*) blue, and (*c*) amethyst in the oxidizing flame, and colorless in the reducing flame?

(3) What is aqua regia, and how is it made?

(4) What are the two methods of qualitative analysis?

(5) Express, in the form of an equation, the reaction that takes place when silver nitrate is precipitated by hydrochloric acid.

(6) Describe the separation of the metals of the third group when phosphoric and oxalic acids are absent.

(7) What metals are precipitated by hydrochloric acid?

(8) What part of the flame of a Bunsen burner acts (*a*) as an oxidizing flame? (*b*) as a reducing flame?

(9) How are (*a*) oxidation and (*b*) reduction accomplished by the flame of a Bunsen burner?

(10) What metal imparts a crimson color to the flame?

(11) What metals give black precipitates when their solutions are treated with hydrogen sulphide?

(12) Describe the method of determining the members of the seventh group.

(13) What metal, when fused with sodium carbonate and potassium nitrate, imparts a deep-green color to the fusion?

(14) Name the metals that are not precipitated from acid solutions by hydrogen sulphide, but are precipitated by ammonium sulphide, giving the color of the precipitate formed in each case.

(15) What metals are precipitated by sulphuric acid?

(16) Describe briefly the best method of distinguishing between solutions of zinc and aluminum.

(17) Express, in the form of an equation, the reaction that takes place when sulphuric acid is added to a solution of barium chloride.

(18) How are precipitates washed?

(19) Define (*a*) reagent and (*b*) reaction.

(20) Name the *group reagents* in the order in which they are used.

(21) What is the most characteristic test for the common organic acids?

(22) When hydrogen sulphide produces a precipitate in the solution of a metal, what compound of the metal is formed?

(23) What metals are precipitated as hydrates by ammonium sulphide?

(24) What is the most characteristic test for bromides?

(25) How are solutions concentrated?

(26) What metals are precipitated in the form of hydrates by sodium carbonate?

(27) What is the best test for ammonium compounds?

(28) What metals are precipitated from their solutions by a large excess of water?

(29) What metals are precipitated as yellow sulphides by hydrogen sulphide?

(30) Give a list of the metals composing each of the groups.

(31) How are the acids divided into groups?

(32) How are cobalt and nickel separated?

(33) (*a*) What is the color of the precipitate formed when a solution of antimony chloride is treated with hydrogen sulphide? (*b*) Express this reaction by an equation.

(34) If a compound is fused with sodium carbonate on the charcoal, and the fusion when placed on a piece of silver and moistened with water produces a black stain on the silver, what is learned of the composition of the compound?

(35) How would you distinguish between barium, strontium, and calcium in solutions?

(36) Briefly describe the most characteristic test for phosphoric acid.

(37) What is indicated when the original fourth-group precipitate is light colored?

(38) Complete the following equation, and name the factors and products of the reaction:

$$MgSO_4 + Na_2HPO_4 + NH_4OH = ?$$

(39) What is the color and composition of the precipitates formed when sodium hydrate is added to the following solutions: (*a*) silver? (*b*) lead? (*c*) mercurous? (*d*) mercuric? (*e*) copper?

(40) What color is imparted to the flame by volatile barium compounds?

(41) Describe the precipitate formed when hydrogen sulphide is slowly added to a mercuric solution.

(42) If a compound, when heated with concentrate sulphuric acid, gives off carbon monoxide and carbon dioxide, and does not char, what acid is indicated?

(43) Solutions of copper and nickel have similar colors. What is the simplest way to distinguish between them?

(44) How would you test for nitric acid in a solution?

(45) Complete the following equation, and name t[he] factors and products of the reaction.

$$2Na_2HAsO_3 + 3H_2S + 4HCl = ?$$

(46) What metals form white precipitates when amm[o]nium sulphide is added to their solutions?

(47) How may ferrous solutions be changed to ferric?

(48) Why is ammonium chloride added to the soluti[on] before precipitating the third group with ammonia?

(49) What metals are not precipitated by ammonium su[l]phide?

(50) What common metals form two series of salts?

(51) What odor is given off when acetates are heat[ed] (*a*) with concentrate sulphuric acid? (*b*) with concentr[ated] sulphuric acid and alcohol?

(52) What metals, when their solutions are treated w[ith] hydrogen sulphide, produce black precipitates that [are] changed to white, insoluble compounds by heating with co[n]centrate nitric acid?

(53) (*a*) When hydrogen sulphide is added to an a[cid] solution of an arsenious compound, what precipitate [is] formed? (*b*) In what is this precipitate soluble?

(54) Complete the following equation:

$$Hg_2(NO_3)_2 + 4H_2SO_4 = ?$$

(55) How does lead behave when heated on the charc[oal] before the blowpipe?

(56) What metal is precipitated from its solutions [by] hydrogen sulphide, in the form of a yellow sulphide tha[t is] insoluble in ammonium sulphide?

(57) Briefly describe the most characteristic test [for] hydrochloric acid.

(58) If a substance, when heated on the charcoal bef[ore]

the blowpipe, gives off white fumes with a garlic odor, what is indicated?

(59) What precipitates are obtained when the following solutions are treated with barium chloride: (*a*) a sulphate? (*b*) a thiosulphate? (*c*) a sulphite?

(60) If the precipitates obtained as described in the last question are pure, how do they act when treated with hydrochloric acid?

(61) How may chromates be reduced?

(62) When hydrogen sulphide is added to a mercurous solution, (*a*) what is the color and composition of the precipitate? (*b*) In what is it soluble?

(63) Describe a blowpipe.

ACTUAL ANALYSIS.

NOTE.—With this Question Paper the student receives twelve 2-ounce bottles of solutions for analysis. About one-third the contents of each bottle should be sufficient for the analysis, but more is given in order that the work may be verified. The student should not attempt to analyze these samples until he is thoroughly familiar with the Instruction Paper, and has analyzed a number of solutions that he has made up himself, for these samples can only be duplicated at the student's expense.

SINGLE METALS.

(64) What metal, in solution, is contained in bottle labeled "Qualitative Analysis, Part 1, Question 64"?

(65) What metal is contained in bottle labeled "Qualitative Analysis, Part 1, Question 65"?

(66) What metal is contained in bottle labeled "Qualitative Analysis, Part 1, Question 66"?

(67) What metal is contained in bottle labeled "Qualitative Analysis, Part 1, Question 67"?

MIXTURES.

(68) What metals are contained in bottle labeled "Qualitative Analysis, Part 1, Question 68"?

(69) What metals are contained in bottle labeled "Qualitative Analysis, Part 1, Question 69"?

(70) What metals are contained in bottle labeled "Qualitative Analysis, Part 1, Question 70"?

COMPOUNDS.

(71) What compound (metal and acid) is contained in bottle labeled "Qualitative Analysis, Part 1, Question 71"?

(72) What compound is contained in bottle labeled "Qualitative Analysis, Part 1, Question 72"?

(73) What compound is contained in bottle labeled "Qualitative Analysis, Part 1, Question 73"?

(74) What compound is contained in bottle labeled "Qualitative Analysis, Part 1, Question 74"?

(75) What compound is contained in bottle labeled "Qualitative Analysis, Part 1, Question 75"?

QUALITATIVE ANALYSIS.

(PART 2.)

(1) What are the principal operations performed in the analysis of substances by the dry method ?

(2) If a white, luminous, infusible mass is obtained when a substance is heated on the charcoal, (*a*) what does this indicate ? (*b*) What should be the next step in the analysis ?

(3) If the infusible mass mentioned in the last question assumes a rose color when ignited with cobalt nitrate, what is indicated ?

(4) (*a*) What is the first step in the examination of urine ? (*b*) How is this accomplished ?

(5) (*a*) What odor is observed when an acetate is heated with concentrate sulphuric acid ? (*b*) What should be the next step in this case ?

(6) How are the alkaloids divided into groups ?

(7) In what form should a substance be, when analyzed by the dry method ?

(8) If a substance heated on the charcoal fuses and penetrates the charcoal, (*a*) what is indicated ? (*b*) How would you distinguish the bases that may be present ?

(9) If a substance is fused on the charcoal with sodium carbonate, and the fusion when placed on a piece of silver and moistened with water produces a black stain, what is indicated?

(10) How may we obtain a solution of a substance that is insoluble in water and acids?

(11) Into what two classes are the phosphates that occur in urine divided?

(12) Name the common volatile alkaloids.

(13) What points should be observed when a substance is heated in the closed tube?

(14) (*a*) What is indicated if a substance deflagrates when heated on the charcoal before the blowpipe? (*b*) What further information is obtained if a residue of chloride is deposited on the charcoal?

(15) What are the principal points to be observed when a substance is heated on the charcoal before the blowpipe?

(16) What metals may be recognized by fusing their compounds on the platinum foil with sodium carbonate and potassium nitrate?

(17) If a substance effervesces when treated with concentrate sulphuric acid, (*a*) what is indicated? (*b*) What should be the next step in the examination in this case?

(18) For what is thorium important?

(19) (*a*) What is the principle of the spectroscope? (*b*) In what cases is it used?

(20) If a substance when heated in the closed tube gives off a gas having the odor of bitter almonds, what is indicated?

(21) What is indicated if a gas having an alkaline reaction and the odor of ammonia is evolved when a substance is heated in the closed tube?

(22) If a substance volatilizes when heated on charcoal, giving off fumes with a garlic odor, (*a*) what is indicated? (*b*) If the substance is yellow, and the odor of burning sulphur is also given off, what additional information is obtained?

(23) If a solid heated with concentrate sulphuric acid gives off a mixture of gases that give a blue flame when ignited, and render a drop of barium hydrate turbid when held at the mouth of the tube, what is indicated?

(24) How are the metals classified with regard to their solubility?

(25) What rare elements belong to Group VII?

(26) Briefly describe the method of determining arsenic in water?

(27) (*a*) What is the reaction of normal urine, and (*b*) how is it determined?

(28) How may strychnine and brucine be separated?

(29) (*a*) What compounds yield carbon monoxide when heated with concentrate sulphuric acid, and (*b*) how is the carbon monoxide recognized?

(30) What rare elements are found in Division B of Group II?

(31) What poisonous metals are most frequently found in water?

(32) How would you test for nitric acid or nitrates in drinking water?

(33) Of what common non-volatile alkaloids is Group II composed?

(34) If a substance, when heated in the closed tube, changes color from white to yellow when hot, and becomes white again upon cooling, what is indicated?

(35) If a substance when heated on the charcoal yields a white, malleable, metallic globule, surrounded with a

dark-yellow, volatile incrustation, which becomes light yellow when cold, and gives a blue tinge to the flame when it is volatilized, what is indicated?

(36) If a substance held on a loop of platinum wire in the Bunsen flame imparts a green color to the flame, what is indicated?

(37) How may gold and platinum be separated?

(38) How may the presence of organic matter in water be detected?

(39) Describe a characteristic test for atropine.

(40) How is the specific gravity of urine determined?

(41) (*a*) How is carbon dioxide recognized when it is evolved from a substance heated in a closed tube? (*b*) What does it indicate?

(42) How does antimony act when heated on the charcoal before the blowpipe?

(43) How do metals impart a color to the Bunsen flame?

(44) How may morphine and cocaine be separated?

(45) For what purpose is a substance heated with concentrate sulphuric acid?

(46) If a substance gives a white sublimate when heated in the closed tube, and deposits a black metallic mirror on the tube when heated with powdered charcoal, what is indicated?

(47) What colors are imparted to the flame (*a*) by barium? (*b*) by strontium? (*c*) by calcium?

(48) If a substance when heated in the closed tube gives off violet vapors that condense in the upper part of the tube, forming a black sublimate, what is indicated?

(49) What compounds of the metals are most suitable for examination by means of the spectroscope?

(50) (*a*) In what two forms does ammonia occur in water? (*b*) How may these forms be determined?

(51) In the examination of solids, if a bromide is indicated, what test should be applied?

(52) If a substance carbonizes when heated in the closed tube, (*a*) what is indicated? (*b*) What further information is obtained if the odor of burnt sugar is given off at the same time?

(53) (*a*) What three metals impart distinctive colors to the borax, or microcosmic, bead? (*b*) What color is imparted to the bead by each of these metals?

(54) (*a*) With what metals is vanadium sometimes associated in nature? (*b*) Give one or two tests by which it may be recognized.

(55) How is nitrous acid determined in water?

(56) Upon what chemical principle does the determination of sugar in urine depend?

(57) (*a*) Can a metal be determined by means of the spectroscope, in the presence of other metals? (*b*) Can more than one metal be determined at once by this method?

(58) If a substance chars and gives off an odor like that of burnt sugar, when heated with concentrate sulphuric acid, what is indicated?

(59) Briefly describe a method for the determination of albumin in urine.

(60) How may lithium be recognized?

(61) Briefly describe a method for the determination of unoxidized phosphorus.

(62) Name the common non-volatile alkaloids.

(63) (*a*) How are the chlorides in urine determined? (*b*) In what cases is this determination important?

(64) Describe the phenomena observed when brucine is treated (*a*) with concentrate nitric acid and stannous chloride; (*b*) with concentrate nitric acid and hydrogen sulphide.

(65) What rare elements belong in Group I?

(66) Between what limits does the specific gravity of urine vary (*a*) in health? (*b*) in disease?

(67) (*a*) Where is titanium found in nature? (*b*) Give a characteristic test by which it may be recognized.

(68) In a case where poisoning by phosphorus is suspected, why would it not be sufficient to treat the sample with an oxidizing agent, and then test for phosphoric acid?

ACTUAL ANALYSIS.

(69) What metal is contained in the box labeled "Qualitative Analysis, Part 2, Question 69"?

(70) What compound is contained in the box labeled "Qualitative Analysis, Part 2, Question 70"?

(71) What metal is contained in the box labeled "Qualitative Analysis, Part 2, Question 71"?

(72) What compound is contained in the box labeled "Qualitative Analysis, Part 2, Question 72"?

(73) What compound is contained in the box labeled "Qualitative Analysis, Part 2, Question 73"?

(74) What compound is contained in the box labeled "Qualitative Analysis, Part 2, Question 74"?

(75) What compound is contained in the box labeled "Qualitative Analysis, Part 2, Question 75"?

(76) What compound is contained in the box labeled "Qualitative Analysis, Part 2, Question 76"?

(77) What double salt is contained in the box labeled "Qualitative Analysis, Part 2, Question 77"?

(78) What powdered mineral is contained in the box labeled "Qualitative Analysis, Part 2, Question 78"?

(79) What fertilizer is contained in the box labeled "Qualitative Analysis, Part 2, Question 79"?

(80) What pigment is contained in the box labeled "Qualitative Analysis, Part 2, Question 80"?

QUANTITATIVE ANALYSIS.

(PART 1.)

(1) How may the subject of quantitative analysis be divided?

(2) When copper is determined as oxide, what reagents may be used to precipitate it?

(3) (*a*) When arsenic is precipitated by magnesia mixture, what is the composition of the precipitate at first formed? (*b*) What change does this precipitate undergo before it is weighed?

(4) State in the form of an equation the reaction that takes place when calcium oxalate is titrated with potassium permanganate.

(5) If a sample of sodium chloride weighing .423 gram is taken for analysis, and the precipitate of silver chloride weighs 1.036 grams, what is the percentage of chlorine in the sample?

(6) (*a*) State briefly how volumetric determinations are made. (*b*) To what three classes of determinations may this method be applied?

(7) In the electrolytic determination of copper, why must the electrode containing the copper be removed from the solution as soon as the electric current is broken?

(8) (*a*) What is the composition of the precipitate formed when hydrogen sulphide is conducted through a solution of antimony? (*b*) How is the correction made for this precipitate?

(9) What is the relative oxidizing effect of a potassium-permanganate solution on iron and calcium oxalate?

(10) In the gravimetric determination of iron, if 1 gram of pure ferrous-sulphate crystals is taken for analysis, and the weight of Fe_2O_3 obtained is .250 gram, (*a*) what per cent. of iron is found? (*b*) What is the error, stated in percentage?

(11) State briefly how a gravimetric analysis is performed.

(12) In what different ways may nickel be determined?

(13) (*a*) How must the precipitate of magnesium-ammonium arsenate be ignited? (*b*) Why is this necessary?

(14) What standard solutions are required for the determination of chlorine, bromine, iodine, silver, and copper, by Volhard's method?

(15) How are samples prepared for analysis?

(16) In the determination of copper as sulphide, (*a*) what is the composition of the precipitate formed when hydrogen sulphide is led through the copper solution? (*b*) What is the composition of the precipitate when weighed?

(17) State what you understand by a normal solution.

(18) (*a*) What methods do you know for the determination of calcium? (*b*) State some of the advantages of each method.

(19) If 30 cubic centimeters of a decinormal silver-nitrate solution are required to precipitate the chlorine in a solution of common salt, what weight of sodium chloride does the solution contain?

(20) Describe a desiccator, and state for what it is used.

(21) (*a*) In what form is magnesium precipitated? (*b*) What change does this precipitate undergo before it is weighed?

(22) In the case of an acid or alkali solution, how is the point of saturation recognized?

(23) How is the indicator used in Volhard's method prepared?

(24) (*a*) Should samples for analysis be weighed directly on the pan of a balance? (*b*) State reasons for your answer.

(25) (*a*) From what kind of a solution is calcium usually precipitated? (*b*) Why is such a solution used?

(26) How is the sulphuric acid in a compound determined?

(27) Why should a sample be dried before weighing for analysis?

(28) When precipitates adhere closely to the vessel in which precipitation is made, how are they removed?

(29) (*a*) In what form is potassium weighed? (*b*) What are the properties of this precipitate?

(30) (*a*) In the determination of magnesium, why should the solution be stirred during precipitation? (*b*) What precautions are necessary in regard to stirring?

(31) Give a brief description of the methods for the determination of nitric acid, mentioning the principles involved.

(32) Express in the form of an equation the reaction that takes place during precipitation in the gravimetric determination of chlorine.

(33) (*a*) In what form is ammonium weighed? (*b*) How may we check the results obtained in this determination?

(34) Why are hydrochloric acid and ammonium chloride added to a solution from which barium is to be precipitated as sulphate?

(35) As arsenic is precipitated as sulphide from a h solution more readily than from a cold one, why not boil th solution while conducting the hydrogen sulphide through it

(36) If exactly 1 gram of pure copper sulphate is take for analysis, what should be the weight of copper oxid obtained?

(37) In the gravimetric determination of chlorine, wh should we avoid heating the solution before precipitation?

(38) Why are precipitates heated before weighing?

(39) (*a*) If the precipitate of barium sulphate wer placed in a crucible together with the filter paper, an ignited at the full power of a blast lamp, would the result be accurate? (*b*) State reasons for your answer.

(40) (*a*) What is a decinormal solution? (*b*) How is generally written?

(41) Explain why CuO and Cu_2S contain the same pe centage of copper.

(42) (*a*) If 20 cubic centimeters of normal sulphuric ac are required to neutralize a solution of sodium hydrate, wh weight of sodium hydrate is contained in this solution (*b*) What weight of metallic sodium does it contain?

(43) In the gravimetric determination of chlorine, wh is the filter ash treated with nitric and hydrochloric acids?

(44) (*a*) What is the composition of the precipitate th is weighed when phosphoric acid is determined gravimetri ally? (*b*) In what other determination is this precipita weighed?

(45) Give an outline of a volumetric method for t determination of ammonia.

(46) (*a*) How is the ignition of copper sulphide pe formed? (*b*) What precautions must be observed in doi this?

(47) When iron is determined gravimetrically, what the composition of the precipitate that is weighed?

(48) (*a*) What difficulty is experienced in the determination of zinc as sulphide? (*b*) How is this difficulty overcome?

(49) What indicator should be used when a solution containing a carbonate is titrated?

(50) What different gravimetric methods are used for the determination of copper?

(51) (*a*) Name the most common indicators used in acidimetry and alkalimetry. (*b*) State how each of these appears in both acid and alkaline solutions.

(52) If free sulphur is thrown out when arsenic is precipitated as sulphide, how may the precipitate be purified?

(53) (*a*) What two volumetric methods are largely used in the determination of iron? (*b*) State some of the advantages of each of these methods.

(54) In the determination of copper in copper sulphate, by the sulphide method, if the precipitate weighs .3 gram, and there is no error in the work, what weight of pure copper sulphate was taken for analysis?

(55) Describe the method of making up a decinormal solution of silver nitrate, to be used in determining chlorine with potassium chromate as the indicator.

(56) When copper is determined as sulphide, why should the precipitate be shielded from the air, and the process hastened as much as possible?

(57) In the gravimetric determination of iron, why is concentrate nitric acid added to a ferrous solution before precipitation?

(58) (*a*) From what kind of a solution is nickel precipitated by electrolysis? (*b*) What can you say of the strength of the electric current to be used in this determination?

(59) In the determination of silver as chloride, the precipitate is the same as that obtained in the gravimetric

determination of chlorine. Why can the silver be precipitated from a warmer solution than the chlorine?

(60) As magnesium-ammonium phosphate dissolves to a greater extent in a solution containing ammonium chloride than in one containing only ammonia, why is ammonium chloride added to a solution from which magnesium is to be precipitated?

(61) Describe two methods of weighing lead sulphate.

(62) Express in the form of an equation, the reaction that takes place when a solution of ferrous sulphate is titrated with potassium permanganate.

(63) Give the name and formula of the precipitate formed when potassium sulphocyanide is added to a copper solution, in the determination of copper by Volhard's method.

(64) Describe a burette.

ACTUAL ANALYSIS.

NOTE.—With this Question Paper the student receives six compounds, in which certain elements are to be determined. These compounds have been carefully analyzed, so that their composition is known, and the student will be graded upon his results; hence, he is strongly advised not to attempt these determinations until he has performed as many as possible of the operations described in the Instruction Paper.

(65) Determine the chlorine in the sample of sodium chloride labeled "Quantitative Analysis, Part 1, Question 65," by two methods, and state the result obtained by each method.

(66) Determine both copper and sulphuric acid in the sample of copper sulphate labeled "Quantitative Analysis, Part 1, Question 66," and state the method used, with the result obtained. Calculate the sulphuric acid as SO_3.

(67) Determine the iron in the sample of ferrous-ammonium sulphate labeled "Quantitative Analysis, Part 1, Question 67," both gravimetrically and volumetrically, and state the result obtained by each method.

(68) What is the percentage of chromium in the sample of potassium bichromate labeled "Quantitative Analysis, Part 1, Question 68"?

(69) What is the percentage of magnesium in the sample of magnesium-ammonium sulphate labeled "Quantitative Analysis, Part 1, Question 69"?

(70) What is the percentage of barium in the sample of barium chloride labeled "Quantitative Analysis, Part 1, Question 70"?

QUANTITATIVE ANALYSIS.

(PART 2.)

(1) What is the principle of the filter pump?

(2) Give the theoretical composition of calcium carbonate.

(3) In determining antimony as sulphide, (*a*) what correction must be made after weighing the precipitate? (*b*) Why is this necessary?

(4) How may the calcium in natrolite be determined?

(5) How may a filter pump be made by means of two large bottles?

(6) Briefly describe two methods of determining manganese in manganous chloride.

(7) In the analysis of German silver, how may the zinc and nickel be separated?

(8) Briefly describe the method of determining water in prehnite.

(9) Describe a filter pump depending on running water.

(10) How would you determine ammonia in ammonium alum?

(11) How is the tin determined in a sample of bronze (*a*) that contains only tin and copper? (*b*) in a sample that contains tin, copper, and lead?

(12) If 1 gram of a substance yields .225 gram of Fe_2O_3 what percentage of FeO does it contain?

(13) (*a*) What device is necessary to prevent breaki the filter when the filter pump is used? (*b*) Describe th device.

(14) (*a*) How would you determine water in ammoni alum? (*b*) What precautions are necessary?

(15) Outline a method for the analysis of an alloy cobalt and nickel.

(16) What weight of lime can be obtained from 2,0 pounds of limestone containing 90 per cent, of calciu carbonate?

(17) (*a*) Describe a Gooch crucible. (*b*) In what cas can it be used?

(18) Describe two methods of separating potassium a sodium.

(19) What are the principal constituents of limestone?

(20) In the analysis of brass, if the sample taken weig .625 gram, and the precipitate of ZnO weighs .1505 gra what percentage of zinc does the sample contain?

(21) What apparatus may be substituted for a Goo crucible in cases where this cannot be used?

(22) How would you determine the silver in a silver coi

(23) Outline a method for the analysis of limesto mentioning only the constituents usually determined.

(24) Give the composition of feldspar.

(25) How would you prepare a Gooch crucible (*a*) to fil coarse precipitates? (*b*) to filter fine precipitates?

(26) State how the copper in silver coins or silverw may be determined.

(27) Give a short method for the determination of carb dioxide in limestone.

(28) In order to save time, how may precipitates that are not easily reduced, be ignited?

(29) (*a*) Of what is brass composed? (*b*) Briefly outline a method for its analysis.

(30) How would you separate the iron and alumina in a sample of limestone?

(31) Give the theoretical composition of magnesium sulphate.

(32) Briefly outline two methods for the analysis of nickel coins.

(33) How may the calcium oxide in compounds be determined?

(34) Give the composition of bronze.

(35) (*a*) What is zinc blende? (*b*) What impurities does it frequently contain?

(36) Describe the method of determining the alkalies in insoluble silicates, such as feldspar.

(37) (*a*) How is the sulphuric acid in a sulphate determined? (*b*) How is it reported?

(38) (*a*) Give the composition of type metal, and (*b*) state how you would dissolve a sample of it for analysis.

(39) Describe the different methods of filtering barium sulphate.

(40) (*a*) Of what are nickel coins composed? (*b*) What impurities do they sometimes contain?

(41) Describe the determination of water in magnesium sulphate, stating what precautions are necessary.

(42) In the analysis of ferrous sulphate, (*a*) in what form is the iron weighed? (*b*) How is it reported?

(43) How is the antimony in type metal determined?

(44) (*a*) What are the chief constituents of chalcopyrite? (*b*) What impurities does it frequently contain?

(45) If a sample of limestone contains 40 per cent. carbon dioxide, how many cubic centimeters of the gas c be obtained from 1 gram of the stone?

(46) How would you calculate the weight of FeO in sample of ferrous sulphate, from the weight of Fe obtained?

(47) What is the composition of Wood's metal?

(48) Outline a method for the determination of iron, zi and manganese in zinc blende.

(49) How is the water in a sample of ferrous sulph determined?

(50) Give a method for the analysis of an alloy compo of bismuth and cadmium.

(51) In the analysis of chalcopyrite, zinc, cobalt, nickel sometimes have to be separated; how may the be precipitated from a solution containing these three met leaving the cobalt and nickel dissolved?

(52) Referring to question 51, (*a*) why is sodium-acet solution added during the precipitation of the zinc? (*b*) W must the amount of sodium acetate added be limited?

(53) What is the theoretical composition of bari chloride?

(54) What weight of antimony will be used in mak 125 pounds of type metal having the composition: le 83 per cent.; antimony, 17 per cent.?

(55) To determine the water in ferrous sulphate, would it not be sufficient to heat a weighed quantity of sample in a crucible, and report the loss in weight as wat

(56) What are the constituents of Babbitt metal?

(57) Describe the determination of magnesium i compound.

(58) Outline a method for the analysis of a pure sam of chalcopyrite.

(59) In the analysis of a silver coin containing 90 per cent. of silver and 10 per cent. of copper, if .8 gram of the sample is taken, what will be the weight of the silver chloride obtained?

(60) Briefly describe three methods of determining carbon dioxide in calcium carbonate.

(61) In the determination of bismuth in alloys, (*a*) what different compounds of the metal are precipitated when the methods given are used? (*b*) In what different forms is it weighed?

(62) If a sample of bronze contains 92 per cent. of copper, and the weight of the precipitate of cuprous sulphide obtained in analyzing it is .952 gram, what weight of sample was taken for analysis?

ACTUAL ANALYSIS.

(63) Make a complete qualitative and quantitative analysis of the chemical compound contained in bottle labeled "Quantitative Analysis, Part 2, Question 63."

(64) Make a complete analysis of the chemical compound contained in bottle labeled "Quantitative Analysis, Part 2, Question 64."

(65) Make a complete analysis of the chemical compound contained in bottle labeled "Quantitative Analysis, Part 2, Question 65."

(66) Analyze the sample of limestone contained in bottle labeled "Quantitative Analysis, Part 2, Question 66," and give an outline of your method of analysis, together with your results.*

(67) Analyze the sample of zinc blende contained in bottle labeled "Quantitative Analysis, Part 2, Question 67," and send an outline of the method employed, with your results.

* Only the constituents usually determined are required.

(68) Make a complete analysis of the sample of brass contained in bottle labeled "Quantitative Analysis, Part 2, Question 68."

(69) Make a complete analysis of a silver coin, and send a description of the coin used, together with your results.

(70) Make a complete analysis of a nickel coin, and send a description of the coin used, with your results.

NOTE.—A dime and a five-cent nickel piece are recommended for questions 69 and 70, respectively, but the student may use any coin he wishes. A description of the coin used must accompany the results, however.

QUANTITATIVE ANALYSIS.

(PART 8.)

(1) On what does the value of an iron ore depend?

(2) What determinations are usually made in the analysis of pig iron?

(3) What is used to dissolve the sample of steel in determining the total carbon by combustion?

(4) Describe the method of determining the alkalies in a sample of clay.

(5) How is a zinc-copper couple prepared?

(6) For what purposes do we analyze iron ores?

(7) Describe the selection of a sample of pig iron.

(8) (*a*) For what is silver sulphate used in the determination of carbon in steel? (*b*) How is it prepared for this purpose?

(9) For what two purposes are samples of water most frequently examined?

(10) Describe a method for the determination of nitrogen as nitrate in a sample of water.

(11) What are the principal determinations made in the analysis of iron ores?

(12) Is pig iron homogeneous?

(13) Should the same sample of coal be used for th determination of moisture and volatile combustible matter

(14) If the results of a water analysis were reported i parts per million, how would you change the report to grain per U. S. gallon?

(15) What poisonous metals are sometimes found i water?

(16) What points should be observed in selecting sample of ore for analysis?

(17) How would you treat a sample of iron drilling before weighing out portions for analysis, in order to fr the sample from sand and scale?

(18) Describe the determination of volatile combusti matter in a sample of coal.

(19) Enumerate the principal determinations made the examination of potable water.

(20) Outline a method for the determination of iron water.

(21) Describe the process known as *quartering*.

(22) Describe a method for the determination of sulph in iron and steel.

(23) Find the weight of coke that can be obtained fro 5,000 pounds of coal having the following composition:

Moisture	1.22
Volatile combustible matter	38.53
Fixed carbon	56.09
Ash	4.16
	100.00

(24) If called on to examine the water of a town suppl state fully how you would collect the sample.

(25) How would you examine a piece of ice to determi its purity?

(26) (*a*) What is the objection to a cast-iron mortar and pestle for grinding iron ores? (*b*) What would you substitute in place of these?

(27) For what purpose is a starch solution used in the determination of sulphur in iron and steel?

(28) Outline a method for the determination of sulphur in coal or coke.

(29) How would you examine the residue obtained in determining the total solids in a sample of water, to learn as much as possible of the character of the water?

(30) What are the principal scale-forming constituents found in water used as a boiler supply?

(31) Of what is clay composed?

(32) Describe a method of preparing an iodine solution for the determination of sulphur in iron and steel.

(33) (*a*) What is Eschka mixture? (*b*) For what is it used?

(34) On what principle does the method employed for the determination of chlorine in water depend?

(35) Under what conditions must a sample of iron ore be pulverized quickly, and why is this necessary?

(36) Briefly describe the determination of insoluble matter and silica in iron ores.

(37) (*a*) Describe the color method for the determination of manganese in iron. (*b*) What advantage has this method?

(38) (*a*) What constituents are injurious in a clay to be used for the manufacture of firebrick? (*b*) What amount of each of these constituents may be present in a first-class clay?

(39) Discuss the significance of chlorine in drinking water.

(40) (*a*) What do you understand by a 100-mesh sieve? (*b*) For what is it used?

(41) Enumerate the methods given for the determination of iron in ores, stating the advantages of each.

(42) What are the principal determinations made in the analysis of steel?

(43) What determinations are usually made in the analysis of clay?

(44) Describe the determination of free and albuminoid ammonia in water.

(45) Describe a method for the determination of phosphorus in steel.

(46) Describe the standardization of a potassium-permanganate solution to be used for the determination of iron in ores.

(47) (*a*) How much combined water does clay ordinarily contain? (*b*) How is it determined?

(48) What do you understand by the term *albuminoid ammonia?*

(49) (*a*) How is the so called *titrating mixture*, used in the determination of iron, prepared? (*b*) For what purpose is it employed?

(50) By means of an equation, express the reaction that takes place when ferric chloride is reduced by stannous chloride.

(51) Describe a reductor, stating for what it is used.

(52) (*a*) What do you understand by the term *absolute water?* (*b*) How is it prepared?

(53) In determining the manganese in an ore by Volhard's method, if 5.5 cubic centimeters of potassium permanganate, each cubic centimeter of which equals .01 gram of iron, are used, what percentage of manganese does the ore contain?

(54) (*a*) For what purpose is potassium sulphocyanide used in the determination of iron? (*b*) How is a solution for this purpose prepared?

(55) State what you know about the different conditions in which carbon exists in steel.

(56) Describe the preparation of Nessler reagent, stating for what it is used.

(57) By means of an equation, express the reaction that takes place when iodine is added to the solution containing sulphur, in the evolution method for the determination of sulphur in iron.

(58) (*a*) For what purpose is potassium ferricyanide used in the determination of iron? (*b*) What precautions must be observed in making up the solution for this purpose?

(59) By what different methods may the combined carbon in steel be determined?

(60) How should the apparatus used in water analysis be cleaned?

(61) By means of an equation, express the reaction that takes place when iodine is liberated from potassium iodide by potassium bichromate.

(62) Describe the color method for the determination of carbon in steel.

(63) Describe the preparation of the naphthyl-amine solution used in the determination of nitrogen as nitrite in water.

(64) Is there any objection to allowing a powdered sample of coal to stand in the air for some time before it is analyzed?

(65) By means of an equation, express the reaction that takes place during the titration when manganese is determined by Volhard's method.

(66) What color is produced when a naphthyl-amine solution is added to a sample of water that contains nitrites?

(67) From what are nitrites in drinking water thought to be derived as a rule?

(68) How would you prepare the solution used to absorb the carbon dioxide generated in the determination of total carbon in steel by combustion?

(69) Discuss the significance of nitrates in potable water.

(70) Describe the preparation of a standard solution of potassium permanganate to be used in the determination of phosphorus in iron or steel.

QUANTITATIVE ANALYSIS.

(PART 4.)

(1) The percentage of hydrocarbon in a sample of beeswax was found to be 15; what is the percentage of ceresin in the sample?

(2) What do you understand by *potential ammonia* in connection with fertilizers?

(3) A volume of gas occupies, at 22° and 771 millimeters pressure, 11.2 liters; what is its true volume at normal temperature and pressure?

(4) How is the presence of sesame oil in other vegetable oils detected?

(5) In an analysis of bleaching powder, to determine its *available chlorine*, 11.5 grams have been analyzed. For the determination, a standardized solution of arsenious acid was used, 1 cubic centimeter of which is equivalent to .0033 gram of chlorine; 50 cubic centimeters of the bleaching powder in a 1,000-cubic-centimeter solution were titrated, and 47.4 cubic centimeters of the arsenious solution were required. What is the percentage of available chlorine in the sample?

(6) What reagent is used to absorb oxygen in gas analysis?

(7) What does the *acetyl number* represent, and how is it determined?

(8) Show, by an equation, how cane sugar is inverted by hydrolysis, and state what the products of this inversion are.

(9) What reagent is used for the clarification of a sugar solution before it is polarized?

(10) Describe the scheme of the Association of Official Agricultural Chemists for the determination of moisture in fertilizers.

(11) How are the chlorides determined in urine?

(12) Describe how hydrogen is determined in gases.

(13) How may gas analysis, in general, be classified?

(14) The total acid number, in an examination of beeswax, was found to be 87.6. Calculate, from this, the amount of paraffin present in the sample.

(15) Determine the iodine number of a fat from the following data obtained from an analysis:

Weight of fat taken	= 1.0214 grams
Quantity of iodine solution used	= 25 c.c.
Thiosulphate, equivalent to iodine used (mean of 2 blank determinations)......	= 39.5 c.c.
Thiosulphate equivalent to remaining iodine	= 13.4 c.c.
Thiosulphate equivalent to iodine absorbed	= 26.1 c.c.

The thiosulphate solution is so standardized that 1 cubic centimeter of it is equivalent to .0122 gram of iodine.

(16) Describe the elaidin test.

(17) A sample of green syrup, containing invert sugar, is polarized, and shows an angle of polarization of $+86°$ before inversion, and, after being inverted, an angle of $-19°$. The temperature during polarization was 27°. What percentage of cane sugar is contained in the sample?

(18) How is phosphoric acid, present in fertilizers, classified?

(19) Can the specific gravity of milk be considered as an indisputable indicator of the quality of milk?

(20) What reagent is used to absorb carbon monoxide in gas analysis?

(21) State how sulphur dioxide may be estimated in gaseous mixtures, such as furnace gases, etc.

(22) What tests would you apply to determine whether an oil is pure olive oil or not?

(23) What does the iodine number indicate in the analysis of fats?

(24) A sample of molasses, containing invert sugar, shows an angle of polarization of $+93°$ before inversion, and of $-22°$ after inversion; the temperature of polarization was 21°. What percentage of cane sugar does the sample contain?

(25) How many milligrams of potassium oxide are represented by 639.4 milligrams of potassium platinichloride?

(26) What are the chief determinations that are made in the analysis of milk?

(27) In estimating the amount of urea in a sample of urine with Hüfner's apparatus, 2 cubic centimeters of urine were taken, and 12 cubic centimeters of nitrogen were obtained. The pressure was found to be 767 millimeters, and the temperature 13°. The specific gravity of the sample is 1.021. What is the percentage of urea in the sample?

(28) A gas, which has been saturated with moisture, is measured at a temperature of 12° and a pressure of 765 millimeters, and it occupies 97 cubic centimeters. What is its true volume?

(29) State how the iodine number of a fat is determine

(30) What does the saponification number indicate in t analysis of fats?

(31) What does the term *coefficient of purity*, used in t analysis of sugar beets, express?

(32) By a sugar examination, 100 grams furnish 95 gra of sugar; furthermore, a cup, with sugar, weighs 26.12 gram the cup alone weighs 21.12 grams; the cup, with sugar, aft drying, weighs 26.01 grams; further, 2.113 grams of sug furnished .028 gram of ashes. What is the composition the sample?

(33) Describe the determination of total phosphoric ac in fertilizers.

(34) What is the average specific gravity of milk?

(35) What are the principal determinations usually ma in quantitative urinary analysis?

(36) By an organic analysis, 1.0152 grams of a substan gave 40.72 cubic centimeters of nitrogen, measured at 1 and 730 millimeters pressure. What percentage of nitrog does the substance contain?

(37) A sample of molasses contains 89 per cent. of ca sugar; its analysis by Meissl and Hiller's method ga .385 gram of copper, 4.25 grams of molasses being used this estimation. How much invert sugar is found in sample?

(38) State how cane sugar may be estimated by means the polariscope in the presence of invert sugar.

(39) What is the normal weight of sugar used with m polariscopes?

(40) Describe the determination of nitrogen by Kjeldal method.

(41) How may such coloring matters as annatto and saffron be detected, when employed in the coloration of butter?

(42) Explain the use of Lunge's nitrometer.

(43) How would you proceed to obtain a standard sodium-thiosulphate solution, 1 cubic centimeter of which is approximately equivalent to 1 cubic centimeter of SO_2?

(44) How is the presence of hydrocarbons, as an adulterant in mineral and vegetable oils, detected?

(45) State how the qualitative test for invert sugar is performed.

(46) How is the sugar extracted from beets for the purpose of analysis?

(47) How many milligrams of potassium chloride are equal to 312.9 milligrams of potassium platinichloride?

(48) Outline Babcock's method for the determination of fat in milk.

(49) How is Fehling's solution made up, and to how much sugar is 1 cubic centimeter of this solution equivalent?

(50) In determining the CO_2 in gases, making 2 estimates a day (600 a year), 50 cubic centimeters of gas at normal temperature and pressure are used in each determination. Of this volume, 20 per cent. were found to be CO_2 in the average. How much KOH would be used annually?

(51) A sample of raw sugar polarizes, before inversion $+69°$, after inversion $-24°$, at a temperature of 22°. For Meissl and Hiller's determination, 3.5 grams of the sample were used, and 315 milligrams of Cu were obtained. What is the percentage of cane sugar and invert sugar in this sample?

(52) A sample of bleaching powder has been analyzed to determine its available chlorine by means of the *iron method;* .323 gram of ferrous iron was added, and it required 24.6 cubic centimeters of potassium-permanganate solution, 1 cubic centimeter of which is equivalent to .004 gram of iron, to oxidize that part of iron not acted on by the bleaching powder. What is the percentage of available chlorine in the sample?

(53) To how many milligrams of potassium sulphate are 163.5 milligrams of potassium platinichloride equal?

(54) The specific gravity of a sample of milk is 1.0328, and the percentage of fat was found to be 2.56. What is the percentage of total solids?

(55) Explain how sugar is determined in urine.

(56) In the determination of sugar in milk, 210.4 milligrams of cupric oxide were obtained. To how much sugar does this correspond?

(57) How is urea determined in urine?

(58) Describe a simple process that may be successfully used for the detection of butter adulteration.

(59) The refractive index of a fat at 33.5° is 1.4652; what is the refractive index at standard temperature (25°)?

A KEY

TO ALL THE

QUESTIONS AND EXAMPLES

INCLUDED IN THE

EXAMINATION QUESTIONS.

It will be noticed that the Keys have been given the same section numbers as occur on the headlines of Examination Questions to which they refer. All article references refer to the Instruction Paper bearing the same section number as the Key in which it occurs, unless the title of some other Instruction Paper is given in connection with the article number.

QUALITATIVE ANALYSIS.

(PART 1.)

(1) See Art. **1.**

(2) (*a*) Chromium; (*b*) cobalt; (*c*) manganese. See also Arts. **55, 59,** and **66.**

(3) Aqua regia is a mixture of concentrate nitric and hydrochloric acids. See Art. **23,** 5.

(4) See Art. **2.**

(5) $AgNO_3 + HCl = AgCl + HNO_3$.

(6) See Art. **101.**

(7) Silver, lead, and mercury in the mercurous condition.

(8) (*a*) and (*b*) See Art. **8.**

(9) (*a*) and (*b*) See Art. **8.**

(10) Strontium. See also Art. **73.**

(11) Silver, lead, mercurous, mercuric, and copper.

(12) See Art. **108.**

(13) Manganese. See Art. **67.**

(14) Ferrous, black; ferric, black; cobalt, black; nickel, black; chromium, green; manganese, flesh color; aluminum, white; zinc, white.

(15) Lead, mercurous, barium, strontium, and calcium

(16) Both metals are precipitated by sodium hydrate, a the precipitate is dissolved in an excess of the reage From this solution aluminum is reprecipitated by ammoni chloride, but not by hydrogen sulphide; while zinc is rep cipitated by hydrogen sulphide, but not by ammonium ch ride. See Arts. **52,** 2 and **63,** 2.

Another good method of distinguishing between them to add ammonium chloride and ammonium hydrate to solution. Aluminum will thus be precipitated from t solution, while zinc will not.

(17) $BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl$.

(18) See Art. **92.**

(19) (*a*) and (*b*) See Art. **4.**

(20) See Art. **94.**

(21) Heating with concentrate sulphuric acid. See A **127.**

(22) A sulphide. See Art. **4.**

(23) Aluminum and chromium.

(24) See Art. **146,** 2.

(25) See Art. **93.**

(26) Antimony, stannous, stannic, ferric, and aluminu

(27) Heating with sodium hydrate. See Art. **81,** 3.

(28) Bismuth and antimony.

(29) Cadmium, arsenious, arsenic, and stannic. So times the sulphide of antimony has a yellowish color.

(30) See Art. **94.**

(31) See Art. **145.**

(32) See Arts. **58,** 6 and **104.**

(33) (*a*) Red.

(*b*) $2SbCl_3 + 3H_2S = Sb_2S_3 + 6HCl.$

(34) This indicates that the compound is a salt of one of the acids of sulphur.

(35) If a solution of calcium sulphate is added, barium, if present, will be precipitated at once, strontium after a little time, and calcium will not be precipitated at all. The solution may be made very dilute, and sulphuric acid used, instead of calcium sulphate, with the same results. The colors imparted to the flame serve well to distinguish between them; or, they may be identified by the method used to separate them. See Art. **105.**

(36) See Art. **146,** 8.

(37) Only manganese and zinc or one of these metals can be present.

(38)
$$\underset{\substack{\text{magnesium}\\ \text{sulphate}}}{MgSO_4} + \underset{\substack{\text{sodium}\\ \text{phosphate}}}{Na_2HPO_4} + \underset{\substack{\text{ammonium}\\ \text{hydrate}}}{NH_4OH}$$
$$= \underset{\substack{\text{magnesium}\\ \text{ammonium}\\ \text{phosphate}}}{MgNH_4PO_4} + \underset{\substack{\text{sodium}\\ \text{sulphate}}}{Na_2SO_4} + \underset{\text{water}}{H_2O}$$

(39) (*a*) Ag_2O, brown.

(*b*) $Pb(OH)_2$, white.

(*c*) Hg_2O, black.

(*d*) HgO, yellow.

(*e*) $Cu(OH)_2$, blue.

(40) Yellowish green.

(41) See Art. **25,** 5. The intermediate colors may not be seen unless the reagent is added carefully, but the white and the black precipitates are always seen.

(42) Oxalic acid. See Art. **126,** 4.

(43) From acid solutions, copper is precipitated by hydrogen sulphide, while nickel is not.

(44) See Arts. **118**, 1 and **146**, 11.

(45)
$$\underset{\text{sodium arsenite}}{2Na_2HAsO_3} + \underset{\text{hydrogen sulphide}}{3H_2S} + \underset{\text{hydrochloric acid}}{4HCl}$$
$$= \underset{\text{arsenious sulphide}}{As_2S_3} + \underset{\text{sodium chloride}}{4NaCl} + \underset{\text{water}}{6H_2O}$$

(46) Aluminum and zinc. Manganese gives a light-colored precipitate, but it is not white.

(47) By the addition of an oxidizing agent, such as nitric acid, bromine water, a permanganate, etc.

(48) To hold the metals of the succeeding groups in solution.

(49) The alkalies and alkaline earths.

(50) Mercury, arsenic, tin, and iron. In one sense chromium also forms two series of salts, as it acts both as a base and an acid, forming chromium salts and chromates. The same may be said of manganese.

(51) (*a*) The sharp, disagreeable odor of acetic acid.
(*b*) The pleasant odor of acetic ether.

(52) Lead and mercury.

(53) (*a*) Yellow arsenious sulphide As_2S_3.
(*b*) Ammonia, ammonium sulphide, ammonium carbonate, and hot concentrate nitric or sulphuric acid, but is insoluble in hydrochloric acid.

(54) $Hg_2(NO_3)_2 + 4H_2SO_3 = Hg_2 + 4H_2SO_4 + 2NO.$

(55) It fuses easily to a bright, metallic globule, giving the flame a pale, bluish tinge, and deposits a yellow volatile incrustation on the charcoal.

(56) Cadmium.

(57) See Arts. **111** and **146**, **1**.

(58) Arsenic, or one of its compounds.

(59) (*a*) White barium sulphate $BaSO_4$.

(*b*) White barium thiosulphate BaS_2O_3.

(*c*) White barium sulphite $BaSO_3$.

(60) When treated with hydrochloric acid, barium sulphate is not attacked; barium thiosulphate dissolves, giving off sulphur dioxide and throwing out free sulphur, which gives the liquid a yellowish color; and barium sulphite dissolves with the evolution of sulphur dioxide.

(61) Chromić acid and chromates are generally reduced by heating with hydrochloric acid and alcohol, or with sulphurous acid; but other reducing agents may be used.

(62) (*a*) Black mercuric sulphide *HgS*, together with some free mercury.

(*b*) It dissolves slowly in hot concentrate hydrochloric acid, and readily in aqua regia.

(63) See Art. **9.**

(64)
(65)
(66)
(67) These solutions should be tested for single metals. They are intended to test the student's knowledge of the section on the "Deportment of the Metals with Reagents."

(68)
(69)
(70) These solutions should be treated as directed for the "Analysis of Mixed Solutions." No. 69 does not contain members of Division B of Group II, and No. 70 does not contain members of Division A of Group II.

(71)
(72)
(73)
(74)
(75) Each of these compounds contains one metal and one acid. The metal should be determined by making use of the reactions described under "Deportment of the Metals with Reagents," and the acid by means of the reactions described for the common acids.

QUALITATIVE ANALYSIS.

(PART 2.)

(1) See Art. **1.**

(2) (*a*) A compound of tin, aluminum, zinc, barium, strontium, calcium, magnesium, silica, or possibly a silicate.

(*b*) A drop or two of cobalt nitrate should be added, and the mass should be again heated in the oxidizing blowpipe flame to the highest temperature obtainable. See also Art. **18.**

(3) Magnesium oxide, or a compound of magnesium that has been reduced to the oxide on the charcoal. See also Art. **18.**

(4) (*a*) and (*b*) See Art. **75.**

(5) (*a*) The pungent odor of acetic acid.

(*b*) A little of the substance should next be heated with concentrate sulphuric acid and alcohol, when an acetate if present will be recognized by the agreeable odor of acetic ether. See also Art. **24.**

(6) The alkaloids are first divided into volatile and non-volatile alkaloids. The non-volatile alkaloids are divided into three groups, as follows:

Group I consists of those alkaloids that are precipitated from solutions of their salts by sodium hydrate, and dissolve in an excess of the reagent. The common ones are morphine and cocaine.

Group II consists of those alkaloids that are precipitated by sodium hydrate, and are insoluble in an excess of the reagent; and are also precipitated by sodium bicarbonate, even from acid solutions. The common ones are quinine, cinchonine, and narcotine.

Group III consists of those alkaloids that are precipitated by sodium hydrate, and are insoluble in an excess of the reagent, but are not precipitated from acid solutions by sodium bicarbonate. The most common ones are strychnine, brucine, and atropine.

(7) In the form of powder or small crystals.

(8) (*a*) and (*b*) See Art. **13.**

(9) A salt of one of the acids of sulphur.

(10) See Art. **29.**

(11) Earthy and alkaline phosphates. See also Art. **82.**

(12) Nicotine and conine.

(13) See Art. **2.**

(14) (*a*) A nitrate or chlorate.

(*b*) A chlorate. See also Art. **12.**

(15) If the substance decrepitates, deflagrates, fuses, or volatilizes; if a metallic globule forms with an incrustation, if a metallic globule forms without an incrustation, if an incrustation is formed without a metallic globule, if a white luminous mass is formed, if a colored mass is formed.

(16) Manganese and chromium. See also Art. **23.**

(17) (*a*) A carbonate.

(*b*) The gas should be tested at the mouth of the tube with a drop of barium hydrate, and then a fresh sample should be treated with hydrochloric acid, and the escaping gas again tested with barium hydrate. See also Art. **24.**

(18) Its oxide, thoria, is the chief constituent used in the mantle of the Welsbach light.

(19) (*a*) and (*b*) See Arts. **60** and **61.**

(20) A cyanide that is decomposed by heat.

(21) An ammonium compound, or possibly a nitrogenous organic compound or a cyanide containing water. See also Art. **4.**

(22) (*a*) A compound of arsenic.

(*b*) Sulphide of arsenic is indicated.

(23) The substance is an oxalate, and is decomposed by the sulphuric acid, with the evolution of carbon monoxide and carbon dioxide.

(24) See Art. **25.**

(25) Lithium, cæsium, and rubidium.

(26) See Art. **72.**

(27) (*a*) It should be slightly acid.

(*b*) By means of two pieces of litmus paper, one of which is faintly red, and the other faintly blue. See also Art. **76.**

(28) See Art. **108.**

(29) (*a*) Some organic compounds and ferrocyanides.

(*b*) It may be recognized by the blue flame with which it burns, when ignited at the mouth of the tube.

(30) Gold, platinum, iridium, molybdenum, selenium, and tellurium.

(31) Lead, copper, and zinc. See also Art. **72.**

(32) See Art. **65.**

(33) Quinine, cinchonine, and narcotine.

(34) Zinc oxide, or a compound which is reduced to zinc oxide by heat. See also Art. **5.**

(35) A compound of lead.

(36) A compound of barium, copper, thallium, molybdenum, or possibly a borate or phosphate. See also Art. **21.**

(37) See Art. **40,** 6.

(38) By evaporating a sample of the water to dryness, and igniting the residue; when, if organic matter is present, it will char, and generally give off a burnt odor. See also Art. **69.**

(39) See Art. **107.** Probably heating with sulphuric acid and potassium dichromate, or with chromic acid, is the most characteristic test.

(40) See Art. **77.**

(41) (*a*) By rendering turbid a drop of barium hydrate.
(*b*) A carbonate or oxalate.

(42) It readily fuses to a metallic globule, and white fumes of the oxide are given off, which form a white incrustation on the charcoal.

(43) The colors imparted to the flame by metals are due to highly heated luminous vapors; hence, the substance must be volatilized before the flame is colored.

(44) See Art. **100.**

(45) To determine the acid of the compound.

(46) This shows that the substance contains arsenic, probably in the form of oxide As_2O_3.

(47) (*a*) Green.
(*b*) Bright red.
(*c*) Brick red.

(48) That the substance is iodine or an iodide.

(49) Volatile compounds must be used; and, as chlorides are usually the most volatile, they are most suitable for this purpose.

(50) (*a*) and (*b*) See Art. **67.**

(51) The substance should be heated with concentrate nitric acid, which decomposes all bromides except silver bromide, setting free reddish-brown vapors of bromine, which condense in the upper part of the tube, forming red globules.

(52) (*a*) An organic substance.
(*b*) Tartaric acid or a tartrate.

(53) See Art. **22.**

(54) (*a*) See Art. **47.**

(*b*) Distinctive reactions may be obtained with the borax bead, and by adding zinc to an acid solution of vanadium.

(55) See Art. **68.**

(56) Upon the fact that sugar is a reducing agent, and reduces the cupric solution, forming red cuprous oxide Cu_2O.

(57) (*a*) and (*b*) See Art. **60.**

(58) Tartaric acid or a tartrate.

(59) See Art. **79.**

(60) See Art. **57.**

(61) See Arts. **88, 89,** and **90.**

(62) Morphine, cocaine, quinine, cinchonine, narcotine, strychnine, brucine, and atropine.

(63) (*a*) and (*b*) See Art. **81.**

(64) (*a*) and (*b*) See Art. **106.**

(65) Thallium and tungsten.

(66) (*a*) and (*b*) See Art. **77.**

(67) (*a*) and (*b*) See Art. **46.**

(68) The oxidizing agent would convert the phosphorus into phosphoric acid; but, as phosphoric acid is a normal constituent of nearly all animal and vegetable bodies, it would be impossible to say whether the phosphoric acid thus found had come from oxidizing free phosphorus or not.

NOTE.—The substances given for analysis are omitted from the Key, but the student will be told whether his analyses are correct or not.

QUANTITATIVE ANALYSIS.

(PART 1.)

(1) See Art. **1.**

(2) Sodium hydrate, or sodium carbonate.

(3) (*a*) Magnesium-ammonium arsenate $MgNH_4AsO_4$.

(*b*) When this precipitate is heated, water and ammonia are driven off, and magnesium pyroarsenate $Mg_2As_2O_7$ is formed.

(4) See Art. **100.**

(5) $1.036 \times 24.73 \div 100 = .2562028$ weight of chlorine. $.2562028 \div .423 \times 100 = 60.57$ per cent. of Cl in sample. As dividing by 100 and then multiplying the result by 100 merely makes extra work without changing the final result, this is always omitted in actual work. This may be stated as follows:

$$\frac{1.036 \times 24.73}{.423} = 60.57. \quad \text{Ans.}$$

(6) (*a*) and (*b*) See Art. **3.**

(7) See Art. **21.**

(8) (*a*) A mixture of antimony sulphide Sb_2S_3, free sulphur, and water.

(*b*) See Art. **60.**

(9) See Art. **100.**

(10) $.250 \times 70 = 17.50$. $17.50 \div 1 = 17.50$ per cent. of iron found. Taking 56 for the atomic weight of iron and

278 for the molecular weight of ferrous sulphate, we hav $(56 \div 278) \times 100 = 20.14$ per cent. of iron calculate $20.14 - 17.50 = 2.64$ per cent. error.

(11) In answering this question the student should giv in his own words, a brief outline of the general method determining substances gravimetrically, from what he h learned in the Instruction Paper and by practice.

(12) As oxide or as metallic nickel. The metallic nick may be obtained either by precipitation and reduction, or b electrolytic deposition. See also Arts. **22** and **24.**

(13) (*a*) and (*b*) See Arts. **58** and **59.**

(14) See "Volhard's Method for *Cl*, *Br*, *I*, *Ag*, and *Cu*.

(15) See Art. **6.**

(16) (*a*) CuS.

(*b*) Cu_2S.

(17) See Art. **71.**

(18) (*a*) and (*b*) See Arts. **38, 39, 40, 41,** and **100**

(19) One cubic centimeter of decinormal silver nitra precipitates .003537 gram of chlorine, which is equivalent .005837 gram of sodium chloride. Hence,

$.005837 \times 30 = .17511$ gram of sodium chloride. Ans.

(20) See Art. **6.**

(21) (*a*) Magnesium-ammonium phosphate $MgNH_4P$

(*b*) When ignited, ammonia and water are expelled, a magnesium pyrophosphate $Mg_2P_2O_7$ is formed.

(22) By means of certain organic compounds, known indicators, which change color when the reaction of the so tion changes. See also Art. **78.**

(23) See Art. **101.**

(24) (*a*) and (*b*) See Art. **7.**

(25) (*a*) and (*b*) See Art. **39.**

(26) See Art. **66.**

(27) If a sample were not dried before making a determination, the result obtained would not represent the percentage of the given element in the compound analyzed, but would represent the percentage of this element in a certain mixture of this compound and water.

(28) See Art. **9.**

(29) (*a*) and (*b*) See Arts. **62** and **63.**

(30) (*a*) and (*b*) See Art. **35.**

(31) See Art. **111.**

(32) $NaCl + AgNO_3 = AgCl + NaNO_3$.

(33) (*a*) and (*b*) See Arts. **64** and **65.**

(34) See Art. **43.**

(35) See Art. **57.**

(36) The weights would bear the same relation to each other as the molecular weights of the compounds; hence, taking the molecular weights of copper sulphate and copper oxide as 249 and 79, respectively, we have

$$249 : 79 = 1 : x. \quad x = .3172. \quad \text{Ans.}$$

(37) See Art. **13.**

(38) Precipitates are heated in order to get them in forms in which their exact composition is known. In every case the heat serves to expel water, and in some cases it changes the precipitate from a compound of variable composition to a weighable compound whose exact composition is known. For instance, when ferric hydrate is heated, it is changed to ferric oxide, and when magnesium-ammonium phosphate is ignited, it is changed to magnesium pyrophosphate, etc.

(39) (*a*) and (*b*) See Art. **43.**

(40) (*a*) and (*b*) See Arts. **71** and **87.**

(41) This relation depends on the facts that the atomic weight of sulphur is twice that of oxygen, and that there are 2 atoms of copper united with 1 atom of sulphur, while there is 1 atom of copper united with 1 atom of oxygen;

hence, the metal and non-metal are united in the same proportion in each case. In the case of cuprous sulphide, we have 126 parts of copper united with 32 parts of sulphur, while in copper oxide we have 63 parts of copper united with 16 parts of oxygen. Multiplying the weights of copper and oxygen in this compound by 2, we have the metal and non-metal united in the ratio of 126 to 32 in each case.

(42) (*a*) As 20 cubic centimeters of normal sulphuric acid neutralize 20 cubic centimeters of normal sodium hydrate, this solution contains the same weight of sodium hydrate that would be contained in 20 cubic centimeters of a normal solution; hence, it is only necessary to calculate what this weight is. As 1 cubic centimeter of normal sodium hydrate contains .04 gram of the solid, 20 cubic centimeters contain .8 gram.

(*b*) Similarly for sodium. According to the definition of a normal solution, 1 liter contains 23 grams of sodium. Then 1 cubic centimeter contains .023 gram, and 20 cubic centimeters contain .46 gram of *Na*.

(43) The nitric acid is added to dissolve the silver, and the hydrochloric acid to precipitate it as chloride, thus replacing the chlorine that has been driven off. See also Art. **12.**

(44) (*a*) See Art. **68.**
(*b*) See Art. **34.**

(45) See Art. **90.**

(46) (*a*) See Art. **18.**
(*b*) See Art. **19.**

(47) See Art. **14.**

(48) (*a*) and (*b*) See Art. **55.**

(49) Methyl-orange.

(50) The oxide method, the sulphide method, and the electrolytic method.

(51) See "Acidimetry and Alkalimetry."

(52) See Art. **57.**

(53) (*a*) and (*b*) See Arts. **94** to **99.**

(54) As a molecule of cuprous sulphide contains 2 atoms of copper, and a molecule of copper sulphate contains but 1, 2 molecules of copper sulphate are required to produce 1 molecule of cuprous sulphide. Bearing this in mind, and taking the molecular weights of copper sulphate and cuprous sulphide as 249 and 158, respectively, we have

$$158 : 498 = .3 : x. \quad x = .9456 \text{ gram. Ans.}$$

(55) See Art. **91.**

(56) See Art. **19.**

(57) See Art. **15.**

(58) (*a*) and (*b*) See Arts. **24** and **25.**

(59) If the solution from which chlorine is to be precipitated is heated, chlorine will be expelled by the nitric acid added with the reagent, and the result will be too low. Silver is not volatilized in this way, and if some of the chlorine of the reagent is driven off, it makes no difference, as enough will be added to precipitate all the silver at any rate.

(60) See Art. **35.**

(61) See Arts. **26** and **27.**

(62) See Art. **94.**

(63) Cuprous sulphocyanide $Cu_2(SCN)_2$.

(64) See Art. **76.**

(65), (66), (67), (68), (69), (70) The percentage of the elements to be determined in the compounds sent for analysis cannot be given, as it will vary somewhat from time to time. A careful record of the composition of each sample is kept, however, and the student will be graded upon his results.

QUANTITATIVE ANALYSIS.

(PART 2.)

(1) See Art. **2.**

(2) CaO = 56 per cent. CO_2 = 44 per cent. See also Art. **21.**

(3) (*a*) The precipitate of antimony sulphide always contains more or less free sulphur and water. These must be expelled from a part of the precipitate after it is weighed, and from the amount of pure antimony compound obtained from the portion of precipitate taken, the amount of antimony sulphide or antimony in the precipitate is calculated. The sulphur and water may be driven off by heating a portion of the precipitate in an atmosphere of carbon dioxide, or a portion of the precipitate may be treated with fuming nitric acid, and the antimony weighed as oxide, after driving off the acid mixture by heat.

(*b*) If a correction were not made by one of the methods given, the water and free sulphur would be weighed as antimony sulphide, and an erroneous result would thus be obtained.

(4) See Art. **121.**

(5) See Art. **3.**

(6) See Art. **22.**

(7) See Arts. **64, 65,** and **66.**

(8) See Art. **132.**

(9) See Art. **4.**

(10) See Art. **30.**

(11) (*a*) See Art. **49.**

(*b*) See Art. **51.**

(12) Fe_2O_3 contains 90 per cent. of FeO; hence, $.225 \times .90 = .2025$ gram of FeO, and as the weight of a constituent divided by the weight of the original substance, and this number multiplied by 100, gives the percentage of that constituent in the substance, $.2025 \div 1 = .2025$. $.2025 \times 100 = 20.25$ per cent. of FeO. Ans.

(13) (*a*) and (*b*) See Art. **5.**

(14) (*a*) and (*b*) See Art. **31.**

(15) Now no method has been given in the text for the analysis of an alloy containing only these two metals, but methods of separating and determining them are given in the analysis of nickel coins (Art. **59,** *et seq.*) and in the analysis of chalcopyrite, and one of these methods may be employed, omitting, of course, the portions referring to other elements. See Arts. **115** and **116.**

(16) As the stone contains 90 per cent. of calcium carbonate, it contains $2,000 \times .90 = 1,800$ pounds of calcium carbonate; and as calcium carbonate contains 56 per cent. of calcium oxide, $1,800 \times .56 = 1,008$ pounds of lime. Ans.

(17) (*a*) and (*b*) See Art. **6.**

(18) See Arts. **32** to **37,** inclusive.

(19) See Art. **87.**

(20) As ZnO contains 80.26 per cent. of zinc,

$.1505 \times .8026 = .1207913$ gram of zinc.

$.1207913 \div .625 = .1933.$

$.1933 \times 100 = 19.33$ per cent. of zinc. Ans.

(21) A porcelain crucible with a perforated bottom similar to a Gooch crucible. This is frequently called a porcelain Gooch crucible. See also Art. **6.**

(22) See Art. **39,** *et seq.*

(23) See Art. **88,** *et seq.*

(24) Feldspar is essentially a silicate of aluminum and potassium with a smaller quantity of sodium, or of aluminum and sodium with a smaller quantity of potassium, and in addition to these constituents, it nearly always contains smaller amounts of iron, calcium, and magnesium. See also Art. **139.**

(25) (*a*) and (*b*) See Arts. **6** and **11.**

(26) See Arts. **40** and **42.**

(27) See Art. **92.**

(28) See Art. **7.**

(29) (*a*) See Art. **43.**
(*b*) See Art. **44,** *et seq.*

(30) They may be separated by fusing the precipitate of iron and alumina with acid potassium sulphate and proceeding as directed in Art. **141,** but it is better to take a fresh sample and proceed as directed in Art. **95.**

(31) See Art. **12.**

(32) See Art. **58,** *et seq.*

(33) See Art. **20.**

(34) See Art. **48.**

(35) (*a*) and (*b*) See Art. **96.**

(36) See Art. **144.**

(37) See Arts. **11** and **12.**

(38) (*a*) It is an alloy of lead and antimony, containing the metals in varying proportions, the percentage of each metal depending upon the kind of type for which it is intended.

(*b*) It is dissolved for analysis by treating a sample of the finely divided alloy with a mixture of equal volumes of concentrate nitric and tartaric acids. See also Art. **54.**

(39) See Art. **11.**

(40) (*a*) and (*b*) See Art. **58.**

(41) See Art. **12.**

(42) (*a*) The iron is weighed in the form of ferric oxide Fe_2O_3.

(*b*) As the iron in the original substance is in the ferrous state, it is reported as ferrous oxide FeO. See also Arts. **17** and **19.**

(43) See Art. **55.**

(44) (*a*) and (*b*) See Art. **109.**

(45) As the limestone contains 40 per cent. of carbon dioxide, 1 gram of it would contain 40 per cent. of 1 gram, or .4 gram of carbon dioxide. 1,000 cubic centimeters (1 liter) of carbon dioxide weighs 1.97 grams; hence,

$1.97 : .4 = 1{,}000 : x$. $x = 203.05$ cubic centimeters. Ans.

(46) As Fe_2O_3 contains 90 per cent. of FeO, the weight of FeO may be obtained by multiplying the weight of Fe_2O_3 by .90; or it may be calculated by a proportion. As 1 molecule of Fe_2O_3 contains 2 molecules of FeO, the proportion would be

$$Fe_2O_3 : 2FeO = \text{wt. of } Fe_2O_3 : x.$$

(47) It is composed of tin, lead, bismuth, and cadmium.

(48) See Arts. **104** to **107,** inclusive.

(49) See Art. **19.**

(50) No scheme is given for the analysis of an alloy containing only these two metals, but a method of separating and determining them is given in the analysis of Wood's metal (Art. **73,** *et seq.*), and the method here given may be employed by omitting the portions referring to other metals.

(51) See Art. **114.**

(52) (*a*) Zinc is present in the solution in the form of chloride, and as it is precipitated as sulphide, the chlorine set free unites with the hydrogen of the hydrogen sulphide,

forming hydrochloric acid. Zinc sulphide is soluble in a solution containing any considerable amount of free hydrochloric acid, and enough acid may be formed during the reaction to prevent the complete precipitation of the zinc. If sodium acetate is now added, the hydrochloric acid unites with the sodium, forming sodium chloride, and setting free acetic acid, in which zinc sulphide is insoluble, and consequently the zinc will be completely precipitated.

(*b*) If enough sodium acetate is added to unite with all the hydrochloric acid, the nickel and cobalt will also be precipitated; hence, care must be taken to leave enough free hydrochloric acid in the solution to prevent the precipitation of these metals. Enough hydrochloric acid to accomplish this may be left in the solution without interfering with the precipitation of zinc.

(53) See Art. **16.**

(54) As the alloy contains 17 per cent. of antimony, the weight of antimony required will be 17 per cent. of the weight of the alloy, or $125 \times .17 = 21.25$ pounds. Ans.

(55) See Art. **19.**

(56) See Art. **78.**

(57) See Art. **10.**

(58) See Art. **109,** *et seq.*

(59) As the sample contains 90 per cent. of silver, and .8 gram of it are taken for analysis, we have $.8 \times .90 = .72$ gram of silver in the sample. As this is all converted into chloride, taking the atomic weights of silver and chlorine as 107.66 and 35.37, respectively, we have

$107.66 : 143.03 = .72 : x. \quad x = .9565$ gram. Ans.

(60) See Art. **21.**

(61) (*a*) Bismuth oxychloride, basic bismuth nitrate, and basic bismuth carbonate.

(*b*) Bismuth oxychloride $BiOCl$, bismuth oxide Bi_2O_3, and metallic bismuth.

(62) As Cu_2S contains 79.82 per cent. of copper, we have $.952 \times .7982 = .759886$ gram of copper in the sample; and as the bronze contains 92 per cent. of copper, this is 92 per cent. of the weight of the sample. Hence,

$.759886 \div .92 = .8295$ gram of sample taken. Ans.

(63), (64), (65), (66), (67), (68), (69), (70) The percentage of the elements to be determined in the compounds sent for analysis cannot be given, as it will vary somewhat from time to time. A careful record of the composition of each sample is kept, however, and the student will be graded upon his results.

QUANTITATIVE ANALYSIS.

(PART 3.)

(1) The value of an iron ore depends on the amount of iron it contains and its freedom from impurities.

(2) The elements usually determined in pig iron are silicon, sulphur, phosphorus, and manganese. Carbon is also determined sometimes, but not as a rule.

(3) An acid solution of the double chloride of copper and potassium. For its preparation see Art. **60.**

(4) See Art. **80.**

(5) A zinc-copper couple is prepared by immersing zinc in a copper-sulphate solution that contains about 3 per cent. of the crystallized salt. See also Art. **114.**

(6) An iron ore is analyzed to determine its value, its fitness for a certain purpose, and the amount of other material that must be charged into the furnace with the ore.

(7) See Art. **28.**

(8) (*a*) Silver sulphate is used to purify the carbon dioxide evolved, by absorbing any hydrochloric acid it may contain.

(*b*) For its preparation see Art. **63.**

(9) Water is most frequently examined to determine its fitness for use either for domestic purposes or as a boiler supply.

(10) See Arts. **114** and **115.**

(11) The determinations generally made in the analysi of iron ores are insoluble matter and silica, iron, phosphoru sulphur, and manganese. Water is also frequently dete mined.

(12) See Art. **28.**

(13) See Art. **67.**

(14) Multiply the number of parts per million by 58,31 and divide the result by 1,000,000, to obtain the grains p U. S. gallon. See also Art. **81.**

(15) Copper, lead, and zinc are probably the poisono metals most frequently found in water in sufficient quanti to be dangerous. Iron probably occurs in water more fr quently than any of these, but usually in insignificant qua tities. Arsenic and chromium are also occasionally found i water, and both are very poisonous.

(16) See Art. **3.**

(17) The sample should be transferred from one paper t another by means of a magnet, thus leaving the sand a scale, which are non-magnetic, on the first paper. For th details of the process see Art. **28.**

(18) See Art. **67.**

(19) The principal determinations made in the examin tion of potable waters are total solids, chlorine, free an albuminoid ammonia, oxygen consumed, nitrogen as nitrit nitrogen as nitrate, and poisonous metals. The hardness also determined sometimes, but, as it has little to do with th quality of a drinking water, this determination is frequent omitted.

(20) See Art. **118.**

(21) See Art. **3.**

(22) See Art. **30** *et seq.*

(23) As coke is composed of fixed carbon and ash, t percentage of coke in the sample is obtained by addi

the percentages of these constitutents; hence, this sample contains 60.25 per cent. of coke. As there are 5,000 pounds of the coal containing 60.25 per cent. of coke, we have $5,000 \times .6025 = 3,012.5$ pounds coke. Ans.

(24) See Art. **83.**

(25) See Art. **125.**

(26) (*a*) When a cast-iron mortar and pestle are used to pulverize iron ores, the iron wears off, especially from the pestle, and, becoming mixed with the ore, gives it a fictitious value.

(*b*) A mortar and pestle of hardened steel, or a bucking board and muller of chilled iron, should be used for this purpose.

(27) The starch solution is used as an indicator. As soon as the iodine has broken up all the hydrogen sulphide, with the formation of hydriodic acid, it begins to unite with the starch, forming blue starch iodide, and thus indicating that the reaction is complete.

(28) See Art. **69.**

(29) See Art. **86.**

(30) The principal scale-forming constituents in water are the carbonates of calcium and magnesium, and calcium sulphate.

(31) Clay is a mixture of silica with the hydrated silicates of aluminum calcium, magnesium, sodium, potassium, and generally a small amount of iron. See also Art. **72.**

(32) See Art. **35.**

(33) (*a*) See Art. **71.**
(*b*) See Art. **69.**

(34) The method employed for the determination of chlorine in water depends on the relative affinity of silver for chlorine and chromic acid. When silver nitrate is added to water containing both a chloride and a chromate, the silver unites with chlorine until all the chlorine is combined with

silver. Any silver added after this, unites with the chromi acid, forming red silver chromate. Consequently, when w wish to determine chlorine in water, we add a chromate as lead in silver nitrate. White silver chloride is formed a first, but, after a time, a red color is developed, showin that enough silver has been added to unite with all th chlorine, and silver chromate is beginning to form. Then knowing the strength of the silver solution and the amoun used, the amount of chlorine is readily calculated.

(35) If the moisture is to be determined in an ore, or the composition of the ore as it is purchased, or charged int the furnace, is wanted, the sample should be pulveriz quickly, for a damp ore will lose moisture, and a very dr one may absorb it from the air during this operation.

(36) See Art. **5.**

(37) (*a*) See Art. **48.**

(*b*) The chief advantages of this method are its simplicit and the rapidity with which it yields results.

(38) (*a*) Iron and the alkalies are injurious on account the relatively low temperature at which they fuse.

(*b*) A first-class clay for this purpose should not cont more than 2 per cent. of ferric oxide, or more than 1 per ce of either alkali.

(39) See Art. **88.**

(40) (*a*) See Art. **5.**

(*b*) It is used at first when the ore is partly pulverized separate the coarse portion from the fine, and, later, enable us, by passing it all through the sieve, to be s that it is all fine enough for analysis.

(41) See Arts. **6, 7, 8,** and **9.**

(42) See Art. **50.**

(43) The constituents of clay usually determined silica, alumina, ferric oxide, calcium oxide, magnesia, a the alkalies.

(44) See Arts. **92** and **93.**

(45) See Art. **52.**

(46) See Art. **10.**

(47) (*a*) Clay usually contains from 6 to 14 per cent. of combined water.

(*b*) For its determination see Art. **74.**

(48) Albuminoid ammonia does not exist in water in the form of ammonia, but is in the form of nitrogenous organic matter, which is broken up when boiled with potassium hydrate and potassium permanganate, yielding an amount of ammonia proportional to the amount of nitrogenous matter in the water.

(49) (*a*) and (*b*) See Art. **15.**

(50) $2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4$.

(51) See Art. **54.**

(52) (*a*) and (*b*) See Art. **95.**

(53) In Art. **27,** it is stated that the value of a permanganate solution in manganese is 29.46 per cent. of its value in iron. The value of 1 cubic centimeter of this solution in iron is .01 gram, and its value in manganese is, therefore, 29.46 per cent. of .01 or .002946 gram. As 5.5 cubic centimeters of permanganate are used, we have $.002946 \times 5.5 = .0162$ gram of manganese in the solution; and, as 1.5 grams of sample are dissolved, and two-thirds of the solution (= 1 gram of sample) are titrated, we find that 1 gram of the sample contains .0162 gram, or the sample contains 1.62 per cent. of manganese. Ans.

(54) (*a*) Potassium sulphocyanide is used to test for ferric iron, in order to be sure that the iron is completely reduced.

(*b*) The solution for this purpose is prepared by dissolving from 5 to 10 grams of the solid in 100 cubic centimeters of distilled water.

(55) See Art. **55.**

(56) See Art. **97.**

(57) $H_2S + I_2 = 2HI + S.$

(58) (*a*) Potassium ferricyanide is used as an indica when an iron solution is titrated with potassium bichroma to show when the iron is completely oxidized.

(*b*) The solution should always be tested for ferrocyan when made up, and a fresh solution should be prepared ev day or two.

(59) See Art. **58.**

(60) The apparatus used in water analysis should cleaned by rinsing it thoroughly with water after each ana sis, and then rinsing it again before another analysis is ma Good tap water is usually sufficiently pure for this purp but if the water supply is not of good quality, the appara should finally be rinsed out with distilled water. Appara used for this purpose should never be wiped with a clo but should be allowed to drain.

(61)

$$K_2Cr_2O_7 + 6KI + 14HCl = 8KCl + 2CrCl_3 + 7H_2O + 3$$

(62) See Art. **59.**

(63) See Art. **110.**

(64) When a pulverized sample of coal is allowed to st in the air, it will give up moisture if damp, and, if dry will absorb moisture from the atmosphere. In additio this, the composition of the sample itself will change; her the powdered sample should be kept in a tightly stoppe bottle, and analyzed as soon as possible.

(65)

$$2KMnO_4 + 3MnSO_4 + 2H_2O = 5MnO_2 + 2KHSO_4 + H_2S$$

(66) When naphthyl amine is added to water contair nitrites, it produces a pink color similar to that of a di permanganate solution.

(67) Organic matter, especially animal matter, contains considerable nitrogen, and, as it decomposes in the water, the nitrogen is partially oxidized, forming nitrites. It is thought that the nitrites in drinking water are generally formed in this way. Nitrites may come from other sources, but this is believed to be the chief source.

(68) See Art. **61.**

(69) See Art. **113.**

(70) See Art. **43.**

QUANTITATIVE ANALYSIS.

(PART 4.)

(1) Using formula **10**,

$$C = \frac{100\,p - 1{,}350}{86.5},$$

and substituting the known values, we obtain

$$C = \frac{100 \times 15 - 1{,}350}{86.5} = 1.734\% \text{ ceresin in sample. Ans.}$$

(2) By "potential ammonia" is meant the nitrogen contained in the fertilizer, that, by the progress of decomposition of the organic matter of the fertilizer, will be transformed into ammonia.

(3) $$\frac{11.2 \times 273 \times 771}{(273 + 22) \times 760} = 10.52+ \text{ liters. Ans.}$$

(4) See Art. **238.**

(5) As 1 cubic centimeter of the arsenious solution is equivalent to .0033 gram of chlorine, 47.4 cubic centimeters are equivalent to $47.4 \times .0033 = .15642$ gram in 50 cubic centimeters of the solution; but 50 cubic centimeters contain .575 gram of bleaching powder, hence the substance contains

$$\frac{.15642 \times 100}{.575} = 27.2\% \text{ of available chlorine. Ans.}$$

(6) See Art. **29.**

(7) See Art. **206.**

(8) $C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6$. Cane sugar is transformed by inversion into glucose and fructose, as is seen by above equation.

(9) Subacetate of lead, prepared as described in Art. **169**, is most generally used.

(10) See Art. **120.**

(11) See Art. **16.**

(12) See Art. **36** *et seq.*

(13) See Art. **2.**

(14) Using formula **9**,

$$P = 100 - \frac{100\,S}{92.8},$$

and substituting the known values, we obtain

$$P = 100 - \frac{100 \times 87.6}{92.8} = 5.6+,$$

which is the amount of paraffin present in the sample.

(15) The percentage of iodine absorbed equals

$$\frac{26.1 \times .0122 \times 100}{1.0214} = 31.174,$$

which would be the iodine number of the fat under examination.

(16) See Art. **218.**

(17) Using formula **7**,

$$R = \frac{100\,S}{142.66 - 13.5},$$

and substituting the known values, we obtain

$$R = \frac{100 \times (86 + 19)}{142.66 - 13.5} = 81.29\% \text{ of cane sugar.} \quad \text{Ans.}$$

(18) Soluble or water-soluble phosphoric acid; citrate-soluble phosphoric acid; citrate-insoluble phosphoric acid.

(19) No. See Art. **81.**

(20) See Art. **29.**

(21) See Art. **9.**

(22) See Arts. **230** and **231.**

(23) The iodine number in fat determination represents the quantity of iodine that a fat is able to absorb, and thus serves as a measure of the unsaturated acids present in the fat.

(24) Using formula **7,**

$$R = \frac{100\,S}{142.66 - \frac{1}{2}t^{\circ}},$$

and substituting the known values, we obtain

$$R = \frac{100 \times (93 + 21)}{142.66 - 10.5} = 86.259\% \text{ of cane sugar. Ans.}$$

(25) 123.979 milligrams K_2O.

(26) Specific gravity, total solids, ash, total proteids, casein, albumin, and sugar.

(27) Using formula **5,**

$$W = \frac{100\,v(P-p)}{760 \times 354.33\,a \times (1 + .00366\,t)},$$

and substituting the known values, we obtain

$$\frac{100 \times 12 \times (767 - 11.2)}{760 \times (354.33 \times 2) \times (1 + .00366 \times 13)} = 1.607 \text{ grams;}$$

and as the specific gravity of the sample is 1.021, 100 cubic centimeters weigh 102.1 grams and the percentage of urea is

$$\frac{1.607 \times 100}{102.1} = 1.573. \quad \text{Ans.}$$

(28) Using formula **4,**

$$V_0 = \frac{V(P-p) \times 273}{760(273 + t)},$$

and substituting the known values, we obtain

$$V_0 = \frac{97(765 - 10.5) \times 273}{760 \times (273 + 12)} = 92.24+ \text{ cubic centimeters. } \textbf{Ans.}$$

(29) See Arts. **204, 205,** and **206.**

(30) The saponification number indicates the number of milligrams of potassium hydrates required to saponify 1 gram of the fatty substance, and, therefore, represents the capacity of saturation of the fatty acids contained in the sample.

(31) See Art. **179.**

(32)

Sugar	95.00%
Water	2.20%
Ashes	1.32%
Foreign organic substance	1.48%
Total	100.00%

(33) See Art. **122.**

(34) The specific gravity of pure milk varies from 1.208 to 1.035; its average is about 1.0319—.

(35) See Art. **58.**

(36) $\frac{40.72 \times 273 \times 730}{(273+12) \times 760} = 37.466$ cubic centimeters. .1 liter of nitrogen at normal temperature and pressure weighs 1.257 grams, hence, 37.466 cubic centimeters weigh 470.95 milligrams, which equals 4.639 per cent. Ans.

(37) The calculation is similar to that explained in Art. **189.** The values for $Cu = .385$, $W = 4.250$, and the percentage of cane sugar, 89 per cent., are known. Before using formula **8,** we must calculate the value for Z and the proportion of $R : I$, in order to be able to find the value for F in the formula.

$$\frac{Cu}{2} = \frac{.385}{2} = .1925 = Z.$$

$$Z \times \frac{100}{W} = .1925 \times \frac{100}{4.25} = 4.529 = y.$$

$$\frac{100\,P}{P+y} = \frac{8,900}{89+4.529} = 95.15 = R.$$

$$100 - R = 100 - 95.15 = 4.85 = I.$$

Then, $R : I = 95.15 : 4.85.$

By consulting Table 5, we find that the vertical column $I = 200$ is nearest to Z (.1925), the horizontal column headed 95 : 5, is nearest to the ratio $R : I = 95.15 : 4.85$. Where these two columns meet, we find the factor 52.6, and we can now make the final calculation by substituting the known values in formula **8.**

$\frac{Cu\,F}{W} = \frac{.385 \times 52.6}{4.250} = 4.764\%$ of invert sugar in sample under examination. Ans.

(38) See Art. **183.**

(39) 26.048 grams pure cane sugar.

(40) See Art. **129.**

(41) See Art. **116.**

(42) See Art. **50.**

(43) See Art. **11.**

(44) See Art. **227.**

(45) See Art. **181.**

(46) See Arts. **176, 177,** and **178.**

(47) 96.029 milligrams PCl.

(48) See Art. **93.**

(49) For the preparation of Fehling's solution, see Art. **78,** *Qualitative Analysis*, Part 2; 1 cubic centimeter of this solution is equivalent to .005 milligram of sugar.

(50) As 50 cubic centimeters of gas are taken, and this, on average, contains 20 per cent. CO_2, the amount of CO_2 in each determination weighs 19.77 milligrams. The absorption of CO_2 by a potassium-hydrate solution is expressed by the equation: $2KOH + CO_2 = K_2CO_3 + H_2O$ and 43.89 parts of CO_2 are absorbed by 112 parts KOH. Then, $43.89 : 112 = 19.77 : x$, when $x = 50.45$ milligrams KOH, and as 600 determinations are made, 50.45 milligrams $\times$ 600 = 30.27 grams, or 30.27 grams of KOH would be consumed.

(51) The first step to be taken is to calculate the percentage of cane sugar; we employ formula **7**,

$$R = \frac{100\,S}{142.66 - \frac{1}{2}t},$$

and substitute the known values,

$$R = \frac{100 \times (69 + 24)}{142.66 - 11} = 70.636\% \text{ cane sugar. Ans.}$$

For the calculation of the invert sugar, we have to calculate the proportion $R : I$, and the value for Z, in order to obtain the value F, which is needed for formula **8.**

The known values are $Cu = .315$, $W = 3.5$, and the percentage of cane sugar $P = 70.636$ per cent.

$$\frac{Cu}{2} = \frac{.315}{2} = .1575 = Z.$$

$$Z \times \frac{100}{W} = .1575 \times \frac{100}{3.5} = 4.5 = y.$$

$$\frac{100\,P}{P + y} = \frac{7{,}063.6}{70.636 + 4.5} = 94.01 = R.$$

$$100 - R = 100 - 94.01 = 5.99 = I.$$

$$R : I = 94.01 : 5.99.$$

By consulting Table 5, we find that the vertical column headed "$I = 150$" is nearest to Z ($= .1575$), and the vertical column 94 : 6 is nearest to the ratio $R : I$ (94.01 : 5.99). Where these two columns meet, we find the factor 51.6, and can now apply formula **8**,

$$\frac{Cu\,F}{W} = \frac{.315 \times 51.6}{3.5} = 4.644\% \text{ invert sugar.}$$

Hence, the sample contains 70.636% cane sugar. 4.644% invert sugar. } Ans.

(52) Since 1 cubic centimeter of standard potassium permanganate corresponds to .004 gram of iron, and 24.6 cubic centimeters correspond to .0984 gram, then, .323 gram of iron taken, less .0984 gram of iron not oxidized by the bleaching powder, equals .2246 gram of iron oxidized by the sample.

Since 56 parts of *Fe* correspond to 35.5 parts of *Cl*, we obtain the proportion:

$$56 : 35.5 = .2246 : x,$$

when $x = .1424$ gram available *Cl*. .4 gram bleaching powder contains .1424 available chlorine. 1 gram contains .356 gram, or 35.6 per cent. Ans.

(53) 58.647 milligrams K_2SO_4.

(54) Using formula **6**,

$$t = \left(\frac{100\ S - FS}{100 - 1.0753\ FS} - 1\right)(250 - 2.5\ F),$$

and substituting the known values, we obtain

$$t = \left[\frac{100 \times 1.0328 - (2.56 \times 1.0328)}{100 - 1.0753(2.56 \times 1.0328)} - 1\right][250 - (2.5 \times 2.56)],$$

when $t = 8.720$.

Then, total solids not fat = 8.720%, and fat = 2.56%; hence, total solids = 8.720 + 2.56 = 11.28%. Ans.

(55) See Arts. **59** and **60.**

(56) As 210 milligrams of cupric oxide equal 168 milligrams *Cu*, referring to Table 3, we find

165 milligrams *Cu*	=	120.20
3 milligrams $Cu \times .75$	=	2.25
168 milligrams *Cu*	=	122.45 milligrams $C_{12}H_{22}, H_2O$.

Ans.

(57) See Art. **64** *et seq.*

(58) See Art. **114** *et seq.*

(59) See Art. **224.** $33.5 - 25 = 8.5$; $.000176 \times 8.5 = .0015$. Then, $1.4652 + .0015 = 1.4667$ refractive index at standard temperature. Ans.